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Nanocomposite gel study of surface-initiated block copolymer by ring-opening metathesis polymerization and lignin-based polymers directly from pyrolysis lignin via RAFT polymerization

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Nanocomposite gel study of surface-initiated block copolymer by ring-opening metathesis polymerization and lignin-based polymers directly from pyrolysis lignin via RAFT polymerization

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Xianglan Bai

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

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ABSTRACT

This thesis introduced two of my research projects: the nanocomposite gels study of surface-initiated block copolymer, and lignin based polymer that directly through pyrolysis lignin. The purpose for the nanocomposite gels study is finding the factors that will affect the gel formation. For the pyrolysis lignin polymerization study, the purpose is to use functionalized pyrolytic lignin directly though polymerization process to obtain lignin based polymer.

The nanocomposite gels study is based on the research results from Sri-Harsha Kalluru's Ph. D work. Kalluru successfully synthesized the exfoliated block copolymer from norbornene and cyclopentene, which could form gel when mixed with tetrahydrofuran and sodium chloride salt. The block copolymer nanocomposite gels used in this work has little difference than the Kalluru's work, 5-Ethylidene-2-norbornene and cyclopentene are two monomers that for nanocomposite block copolymer synthesis. As conducted gel tests of various nanocomposites, the nanocomposite only in certain molecular weight and 5-Ethylidene-2-norbornene fraction range can form gel. The salt and polymer concentration effects were different for different nanocomposites. Also, the kinetics tests showed the gel formation process as the stirring time increased.

The lignin based polymer study demonstrated the process of modifying pyrolytic lignin to functionalized lignin that could be used to make lignin based polymer. The hydroxyl groups in pyrolysis lignin were first modified by methacrylate groups before the polymerization process, methacrylate groups can provide the double bonds during the polymerization process. Free radical polymerization and Reversible addition-fragmentation

chain transfer polymerization were used for poly(lignin methacrylate) synthesis. The more controllable RAFT polymerization was chose for synthesizing lignin methacrylate polymer. To avoid the inhibition during the polymerization process, acetylation process is necessary to convert excess hydroxyl groups to acetate groups in the lignin methacrylate. The Functionality 1 lignin methacrylate were used as monomers for poly(lignin methacrylate) synthesis, the derived polymer were tested though GPC, TGA, and DSC for characterization.

CHAPTER 1. INTRODUCTION AND BACKGROUND

PART – A: Nanocomposite Gel

General introduction

With the over many decades researches on the polymeric gels,[1] the polymeric gels have playing an essential role in many applications due to its mechanical and thermal properties.[2] Polymeric gel has cross-linked network structure that with fluid filling in its interstitial space. Unlike most common dry and hard industrial materials. The soft and wet solid like polymeric gel exhibits the capability of undergoing large deformations.[3,4] By different fluids filling in the interstitial space, polymeric gel can be classified as different types. Most studied polymeric gel in nowadays is solid-liquid type.[3] On the other hand, polymer nanocomposites are hybrid materials wherein a nanometer-scale inorganic filler is dispersed in an organic polymer matrix. Appropriately designed polymer nanocomposites have advantages of improved thermal, mechanical and barrier properties compared to non-filled polymers.[5,6] Therefore, in recent years, scientists have focused on studying the nanocomposite gels (NC gels). Nano-clay based inorganic fillers have found wide usage because of their established intercalation chemistry, good cation exchange capacity, and natural availability.[7] Also, clay-based nanocomposite gels showing better mechanical properties over the conventional polymeric gels.[8,9] NC gel has played an increasingly important role in chemical, physical, and biological applications,[5,6,8-23] such as immobilization,[11] drug release and delivery,[13,20,23] electrochemistry,[14,15] tissue engineering,[21] and biomedics.[8,16] The water based NC gel, called NC hydrogels, has special mechanical and thermal properties, as well as favorable deswelling kinetics.[2,9,10,14,15,17]

There are two kinds of gelation: chemical gelation and physical gelation.[3] The most recent and common method of preparing the nanocomposite gel can be found in Haraguchi's research.[24] Nanocomposite gels based on clay are mechanically stable materials, usually formed via crosslinking mechanism where the polymer is crosslinked in order to form a networking structure,[10] which is known as chemical gelation. Haraguchi et al. have introduced a different type of hydrogels where in the hydrogel was not formed via crosslinking mechanism. Polymer grows on the nano-clay's surface by initiating polymerization, then connecting neighboring polymer-clay sheets to form network structure.[24-26] Furthermore, Sri-Harsha Kalluru in Eric Cochran's research group found the surface-initiated block copolymer (SI_BCP)[7] will form gel after mixing with tetrahydrofuran (THF) and sodium chloride (NaCl). Unlike most of the other NC hydrogel that exists, this type of gel is not cross-linked. After drying all the THF in the NC gel, the dry polymer can be dissolved in THF, and the gel will reform.

Ring opening metathesis polymerization (ROMP)

Metathesis is reaction that breaking the existing double bonds then creating new double bonds, ROMP can be also explained as the polymerization that has ring opening mechanism involved with olefin metathesis. ROMP acts as one kind of living/controlled polymerization, which the initiation process happened instantly and the chain propagation process can be controlled. To achieve higher rate and good control of the ROMP reaction, ROMP catalysts should contain transition metal center with ligand system.[27-29]. As showed in Figure 1.1, the ROMP catalyst reacts with the monomer to form a metal carbon double bond

during the initiation process. Then, more monomers attach to metal center to form longer chain during the propagation process.

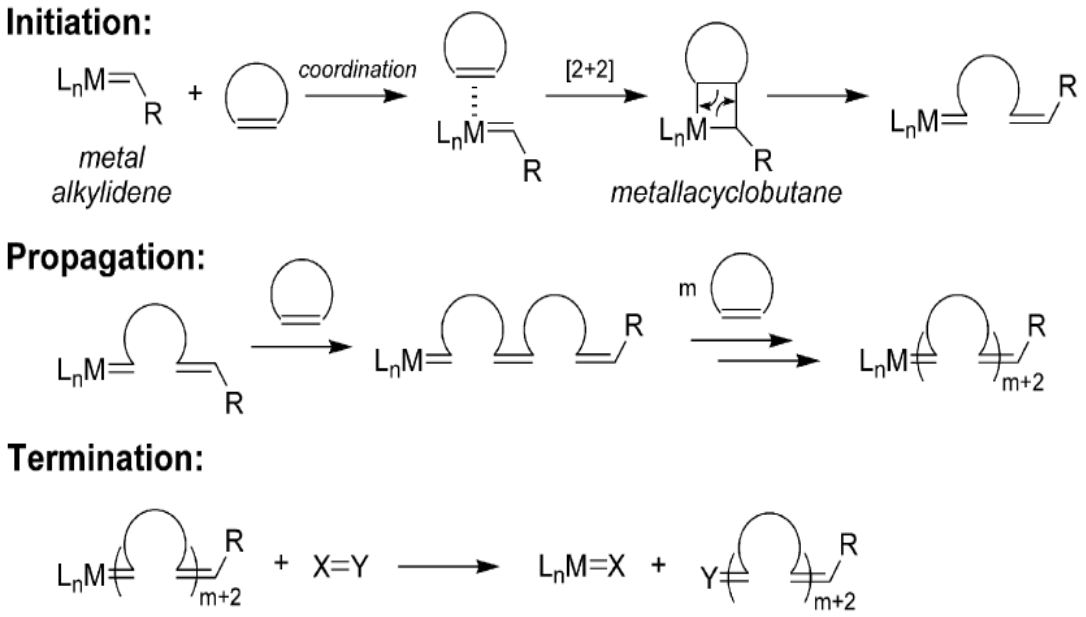

Figure 1.1 The schematic of ROMP,[29] M represents the metal center, Ln represents the ligand system. *Directly cited from Fig. 2. in published article "Living ring-opening metathesis polymerization" by Bielawski, and Grubbs.

There are many kinds of ROMP catalysts, which have different metal centers and different ligand systems. The reason of choosing ligands is reported by Schrock and Grubbs. They designed the ROMP catalysts with ligand system, which largely improved the mechanistic analysis and catalytic activity control.[30] Also, the ligand systems provides better initiation process and propagation process control. Based on the air and moisture sensitivity, functional groups of monomers, and polarity of solvents. There are different choices of metal centers, such as: titanacyclobutane and tantalacylobutane complexes, tungsten-carbene complexes, molybdenum complexes, ruthenium-carbene complexes, etc.[30] There are two most popular types of ROMP catalyst: Schrock catalyst that has molybdenum or tungsten

metal center, and Grubbs catalyst that has ruthenium metal center. The Schrock catalyst is tolerated limited range of functionality groups, and the reaction need to protect from air and water. However, the Grubbs catalyst has broader tolerance range of functionality groups, and better tolerance of air and moisture sensitivity.[31]

Kalluru reported the synthesis procedures of SI_BCP by using norbornene and cyclopentene, the ROMP catalyst used in the reaction is Grubbs first generation catalyst.[7] As mentioned above, the Grubbs catalysts have better tolerance of air and moisture, also with broader range of tolerance of functionality groups. Therefore, the Grubbs catalysts will be a better choice for the reaction. There are different generations of Grubbs catalysts, consider the molecular weight distribution of Poly(norbornene), the Grubbs first generation catalyst $[(PCy_3)_2(Cl)_2Ru{=}CHPh]$ has been choosing. Moreover, the Grubbs first generation catalyst gave low poly dispersity index (PDI) on poly(norbornene) synthesis compare to Schrock catalyst.[32] The monomers used in this work are 5-Ethylidene -2-norbornene (ENbn), and cyclopentene (CPE), which are different than the monomers mentioned in Kalluru's article. Because the ENbn has similar properties with norbornene, also much easier preparation and cleaning processes for the polymerization. In this work, ENbn replaced norbornene as the monomer for first block of SI_BCP synthesis. Because CPE has low ring strain and the ROMP for CPE is difficult, but Trzaska et all. have reported using Schrock catalyst to synthesize low PDI block copolymer when used CPE as one of the monomers.[33] As illustrated in Kalluru's article, the Grubbs first generation catalyst can also been used to synthesize poly(cyclopene) and block copolymer under certain reaction conditions.[7] Kalluru also mentioned about using tricyclohexylphosphine as the co-catalyst in the reaction.[7] When used Grubbs first generation catalyst for the ROMP of CPE, there is side reaction called

acyclic diene metathesis (ADMET), which will form oligomers to affect the PDI and inhibit polymer to achieve high molecular weight. The co-catalyst acts as excess of ligand, the appearance of co-catalyst in the reaction could shift the equilibrium toward polymer product direction, and control the polymerization rate effectively.

Nanocomposites block copolymer synthesis

Nowadays, in nanocomposites polymer synthesis field, montmorillonite (MMT) is most commonly used layered silicate.[34] The isomorphic substitution of sodium and magnesium atoms on the MMT could make the layers have charges, which the influence of Van der Waals and electrostatic forces resulted in creating inter gallery spacing.[35] MMT that with sodium ions on the layers (Na-MMT) was used in this work, because the Na-MMT has excellent cation exchange capacity that would be suitable for the organic modifications.[35,36] In this work, the sodium ions were replaced by certain kind of surfactant to increase the inter gallery spacing.

The alkyl ammonium is one kind of the popular surfactant for the surface modification, because of its long carbon chains, the surface energy will be reduced when the alkyl ammonium surfactant attached to the surface. As reported by Simons et al., by achieving the exfoliation of MMT in nanocomposites polymer via in-situ polymerization, surfactant should has following properties: including ammonium group at head or tail of the surfactant, length of the alkyl chain, and including the polymerization groups in the surfactant.[37] The synthesis procedures and the structure of the alkyl ammonium surfactant that used in this work are showing in Figure 1.2.

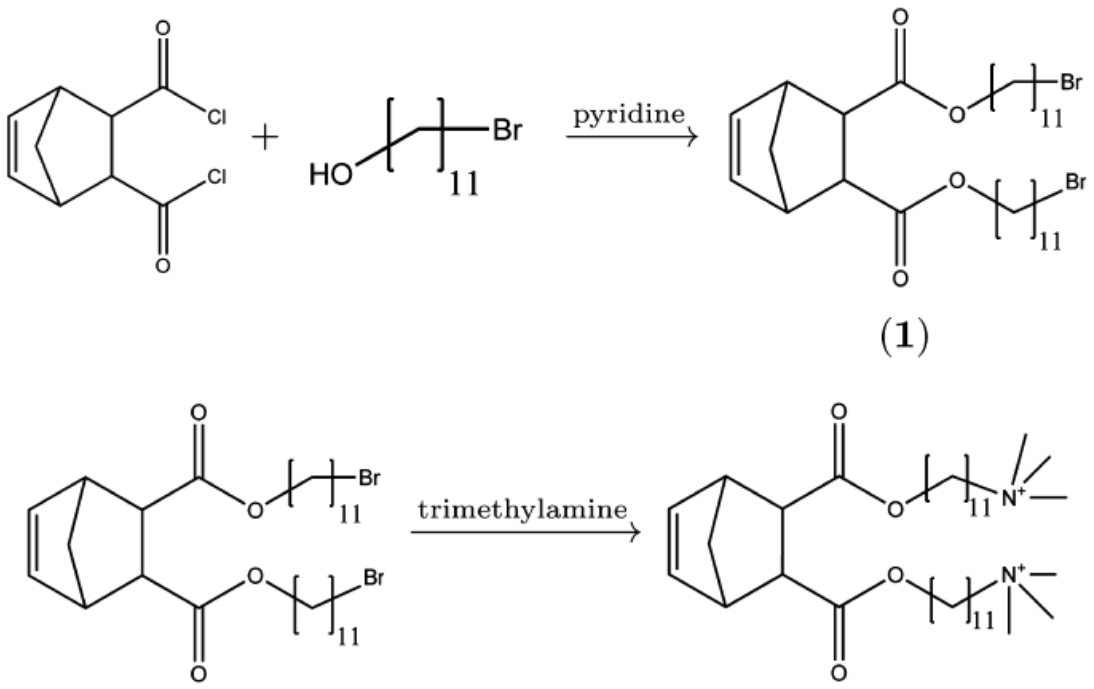

Figure 1.2 Synthesis of norborene-terminated alkylammonium surfactant[7].
*Directly cited from Scheme 1. in published article "Synthesis of Polyolefin/Layered Silicate Nanocomposites via Surface-Initiated Ring-Opening Metathesis Polymerization" by Kalluru, and Cochran.

The surface initiated polymerization (SIP) was very successful for getting exfoliated structures, and this method was developed and demonstrated by many other researchers.[38-40] Also SIP is good method to control the polymer brushes growth that attached on the surface.[28,41] Additionally, the SIP method is suitable for variety of polymerization synthesis types. Therefore, the SIP is most suitable for the nanocomposites block copolymer synthesis in this work. Researchers already successfully synthesized the nanocomposites with norbornene as monomer via surface-initiated ring opening metathesis polymerization (SI-ROMP),[41,42] the addition of another monomer to the polymer brushes will make the structure more exfoliated, because of the larger size of block copolymer brushes of and larger inter gallery spacing. Therefore, the nanocomposites block copolymer synthesized via SI-ROMP methods could be highly exfoliated.

PART – B: Lignin-derived Polymers

General introduction

Because of the limitation of the petroleum resources on the planet, use bio-based materials for polymer synthesis became popular in the polymeric materials field. Lignin is one of the bio-based materials that used in polymer synthesis and bio-based resin in past few decades. Lignin acts as the second most abundant polymer in nature, which has high annual production rate in industries, but large amount of lignin was burned for low-value energy.[43-51] Due to its recyclable and renewable properties, there has been increasingly number of lignin researches in nowadays. Three major phenolic compounds (cinnamyl alcohol) formed lignin: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.[43,44,52,53] Depends on the compositions of these three major cinnamyl alcohol, lignin can be classified as hardwood lignin and softwood lignin. The three-dimensional cross-linked structure make lignin almost impossible to directly polymerize. However, the plenty hydroxyl groups on lignin molecular are suitable resources for chemical modification.[45,54] After introducing functionalized groups, lignin-based monomers can be synthesized to polymer with tunable thermal and viscoelastic properties.[55]

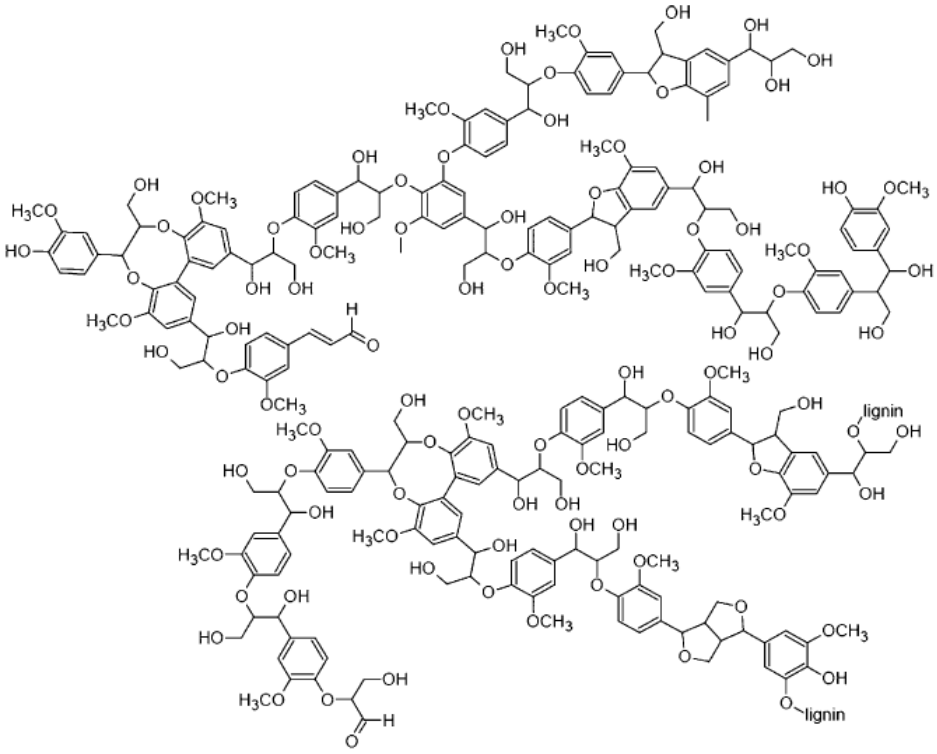

Figure 1.3 General structure of lignin[56-58].
*Directly cited from Figure 1. in published article "Lignin Model Compounds as Bio-Based Reactive Diluents for Liquid Molding" by Stanzione, Sadler, Scala, and Wool.

Pyrolytic lignin

Pyrolytic lignin is a product from pyrolysis oil.[59] The limitation of the petroleum fuel, scientists considered to make the pyrolysis oil as a replacement fuel.[59,60] Comparing to other types of lignin, pyrolysis lignin contains more small molecular weight compounds, and has higher carbon content.[61] But, the pyrolytic lignin includes many reactive functional groups, such as carbonyl groups, hydroxyl groups, etc.[62,63] which makes the pyrolytic lignin not thermal stable at room temperature, and not easily for storage. Typically saying, the pyrolysis process is heating process without oxygen, there are two types of pyrolysis processes: slow pyrolysis and fast pyrolysis. The slow pyrolysis process requires long vapor residence time and undergoes slow heating rate, the liquid product is only about 30 wt%. The

fast pyrolysis process requires short vapor residence time, and uses much higher heating rate than the slow pyrolysis process. The liquid product of the fast pyrolysis process can reach 75 wt%.[64] Gas chromatography mass spectrometry (GC/MS) acts as commonly used method for pyrolytic lignin composition analysis. Figure 1.4 shows the main phenolic monomers in the pyrolysis lignin that used in this work, which is one kind of pyrolysis lignin. The monomer composition will be different for different types of raw materials after pyrolysis. But, the monomers in different types of pyrolysis lignin has one common structure: almost all the monomers contain the at least hydroxyl group, which can be used for further modifications, such as: methacrylation, acrylation, etc.

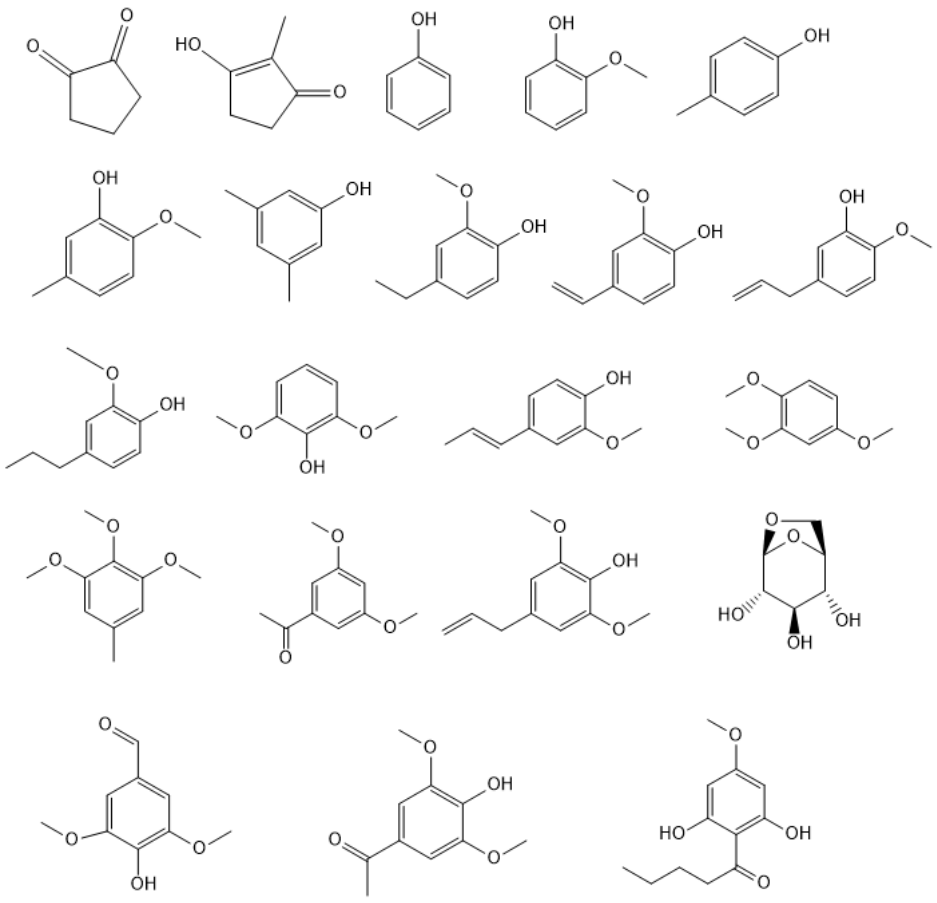

Figure 1.4 Major phenolic monomers from Qu's pyrolysis lignin analysis[63].
*Modified and cited from Fig. 2. in published article "Repolymerization of pyrolytic lignin for producing carbon fiber with improved properties" by Qu, Xue, Gao, Rover, and Bai.

Reversible addition-fragmentation chain transfer (RAFT) polymerization

RAFT is one kind of living/controlled polymerization, which is also requiring the initiation process as the traditional free radical polymerization, commonly used initiators are azobisisobutyronitrile (AIBN), 1,1'-azobis(cyclohexanecarbonitrile) (ACHN), etc.

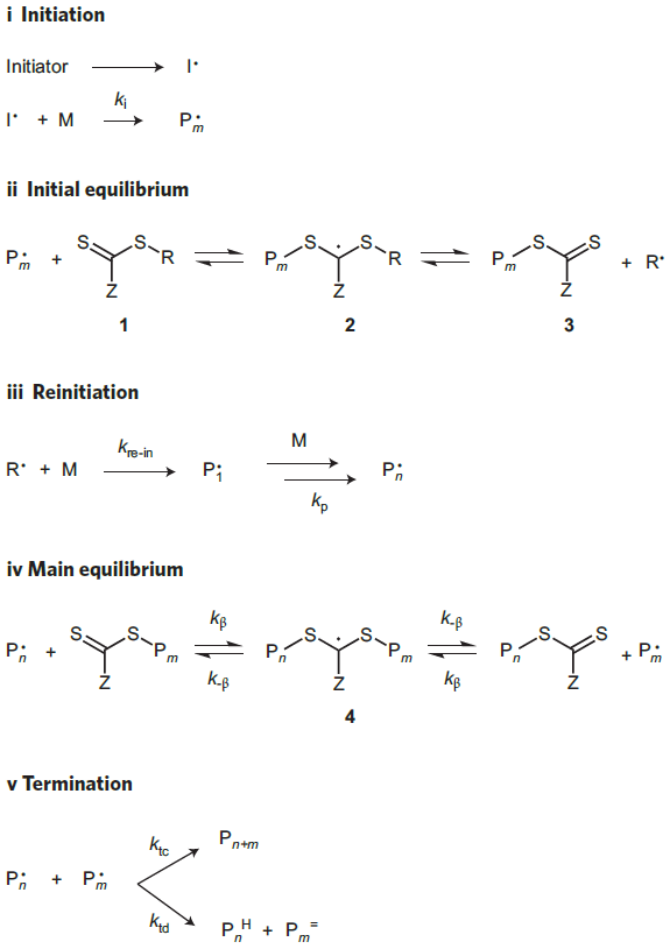

Figure 1.5 The schematic of RAFT polymerization[65].
*Directly cited from Figure 1 in published article "'Green' reversible addition-fragmentation chain-transfer (RAFT) polymerization" by Semsarilar and Perrier.

Unlike the traditional free radical polymerization procedures, RAFT polymerization incorporates with chain transfer agent (CTA), CTA plays a very important role in the RAFT polymerization. Typically, di-thio carbonyl or tri-thio carbonyl compound will be used as the

CTA in RAFT polymerization, like Structure 3 in Figure 1.3. The R group in CTA is also called leaving group, which can be served as the free radical in the reinitiation process. The addition and fragmentation rate of R group in the equilibrium process can be affected by the Z group, Z group will also affect the CTA's stabilization. As showed in Figure 1.3, in the equilibrium process the propagating radicals attaches the carbon-sulfur double bond, the dormant radicals side make the other side becomes free radicals. Then the leaving free radicals undergoes reinitiation process, which will grow longer chain and becomes new propagating radicals. The repeating of the reinitiation and equilibrium processes of propagating radicals happens through the whole reaction. The equilibrium process of propagating radicals and dormant radicals provides equal opportunity of polymer chains to grow. Therefore, the controllable molecular weight and low PDI of polymer products can be achieved via RAFT polymerization.

CHAPTER 2. REVIEW OF LITERATURE

PART – A: Nanocomposite Gels

The nano-clay acts as the crosslinker during the formation of NC hydrogels; this unique gelation mechanism increases the hydrogel's properties, such as swelling and deswelling behaviors, tensile strength, and transparency.[25] A convention of forming polymer gels is using chemical-bonded crosslinker. Due to the expense of some crosslinkers, morphological homogeneity, and the need for significant mechanical properties, nano-clay is now studied as a crosslinker in many NC hydrogel studies.[49,50] Gel is a network structure that the polymer grows on the clay surface by initiating polymerization – connecting neighboring polymer-clay sheets.[25] According to Haraguchi and Takehisa's research polymeric hydrogels (OR gels) that use organic crosslinkers, the amount of crosslinking units are about 750 times large than the organic-inorganic hydrogels that use inorganic clay as the crosslinker.[25] This result in the need for fewer crosslinking units in the NC hydrogel, and makes the polymer chains attached to the clay more flexible. After Haraguchi and Takehisa prepared the organic-inorganic NC hydrogels of poly (N-isopropylamide)-clay, other researchers also started focusing on this water based monomer, which could form NC hydrogels during the polymerization when mixing with nano-clay. The improvement of other physical properties was also mentioned in Haraguchi's more recent paper.[24]

To achieve better physical properties of the NC hydrogel, the nano-clay concentration should not be very high. Aalaie's research focused on the NC hydrogels that are formed using sulfonated polyacrylamide (PAMPS) as the polymer and chromium triacetate as the cross-linker and sodium montmorillonite as the hydrophilic clay.[66] Analysis

of the limiting storage modulus (G'u), indicates that G'u decreases when the clay concentration increases, which is because of the effect of the interactions between polymer chains and the clay surface, and/or between the crosslinker ion and the clay layer. But, above 1000 ppm clay concentration, G'u begins to increase as the clay concentration increases. That indicates a stronger interaction between polymer chains and clay and/or interaction between the clay sheets. The effect of clay concentration on G' values is also supported in other research.[4,17,52-54] Haraguchi and Takehisa agree that the higher the clay concentration, the more crosslinking units appear in the gelation system.[25] Therefore, for the high clay concentration NC hydrogel, the interaction between the crosslinking units and polymer chains is not the only factor that influences the gel formation. The interaction between the clay sheets can also affect the gelation mechanism.

Furthermore, under the new synthesis method, which was stated in Fukasawa's paper,[67] NC gel can be prepared at a low clay concentration. When tested the tensile moduli increases as the clay concentration increases. After a certain point, the further increase of the clay concentration causes the modulus decrease. This result is different from other research articles' findings between the tensile modulus and clay concentration relationship.[2,10,14,15] The small amount of clay effectively acts as crosslinker and interacts properly in the NC gel network, so the tensile properties increase as the clay concentration increases. After the clay concentration reaches certain point, any additional clay added to the system, affects the network structure because of the interaction between excess amounts of clay and monomer. This causes the decrease of the tensile properties when the clay concentration increases. The concentration of polymer also has the influence on the tensile properties and elongation, these two mechanical properties increase as the polymer concentration increases.[67]

Time, the presence of salt, and the clay concentration will all affect the gel formation process. According to Haraguchi, clay concentration has an effect on the viscosity of aqueous clay suspension as well.[26] It was shown that with a higher clay concentration, the viscosity of the aqueous clay suspension also increased.[26]Also as the time increases, the viscosity of the aqueous clay suspension will increase. Moreover, Haraguchi also found that the viscosity of an aqueous clay suspension increased with the addition of salt because of the ionic bond between the clay and the salt.[26] By comparing the salts with different cation valency, he concluded that an increase in viscosity was proportional to the cation valency and that the addition of salt accelerated the sol to gel transition. Haraguchi also demonstrated that nonionic connection between clay and particles has less of an effect on the viscosity of the aqueous clay suspension. The dipolar NIPA molecules dramatically depressed the viscosity of the aqueous clay suspension, because of the mild connection between the NIPA molecules and clay platelets, so that the surrounding NIPA molecules prevent the clay platelets from connecting to each other to form a "house-of-cards" structure.[26] Also, the viscosity of the aqueous clay suspension will be affected by the time and the addition of salt.

For exfoliated polymer/layered silicate nanocomposite (PLSNC) synthesized by Kalluru,[7] the nano-clay is the filler of the NC, and the clay is modified by adding the surfactant on the surface of clay using surface-initiated polymerization method. Then norborenen first added to the long surfactant chain via ring-opening metathesis polymerization method,[29] CPE added as second block by using the same polymerization method.[7] Kalluru had optimized the reaction conditions of SI_BCP synthesis process, which provide an efficient way to make SI_BCP in different molecular weight and different block fractions. Unlike the NC gels preparation methods from other research papers,[24-26,66-70] the

polymer chains already attached on the nano-clay. Therefore, simply adding the solvent, polymer, and salt (or without salt) can be the NC gel preparation method of this kind of polymer.

The published articles on the NC gels indicated that different kinds of monomers were used in the NC gel system, also the researchers are continually working on synthesizing and optimizing the synthesis conditions of NC gels that have better physical properties for use in industrial applications. However, the NC gel still facing the following problems: permeant crosslinking network structure and relatively high polymer concentration in the NC gel. Making the NC gel by using SI_BCPs[7], THF and NaCl is an easier way than methods explained in other research articles. Moreover, for each SI_BCP, there is only approximately 3 wt% of nano-clay loaded. Then, the concentration of clay in NC gel is relatively small. However, until now, the SI_BCP made by Kalluru only could form gel in THF solution. The challenge will be making NC hydrogel, understanding certain situations of gelation and gelation mechanism.

PART – B: Lignin-derived Polymers

The demand of the polymer product has been increasing every year around the world, considering the global issues, continuous using petroleum chemicals to synthesize the polymer products in a not sustainable method in the future. Therefore, bio-based chemicals will become a new chapter for polymer synthesis. The importance of the renewable bio-based materials has also been claimed by the U.S energy and agriculture departments, they expected that 25% of the general chemical products and materials will be made from bio-based materials in 2030.[44] Except the carbon dioxide in the atmosphere, the lignocellulosic

biomass is another most accessible carbon-based raw materials. And lignin is one of the major component of lignocellulosic biomass, which takes 15-50% portion in lignocellulosic biomass.[44,71] Therefore, lignin or lignin-based chemicals could become potential resources to replace the petroleum-based chemicals for future materials synthesis, due to its renewable and low-cost properties.

There is research showed that the benefit of adding lignin in the animal feed, sulfur-free lignins add into animal feed have prebiotic effects that could help grow the beneficial bacteria in the intestines of monogastric animals.[54] The other direct using of lignin in the polymer synthesis is used as a macromonomer. The hydroxyl groups of lignin can be treated as linker for creating lignin-based macromonomers.[44,47] This method is used for synthesizing different kinds of polymer products, such as: polyurethanes,[47,72-77] polyesters,[76-81] etc. One way to synthesize the polyurethanes is using isocyanate reacts with hydroxyl groups of lignin to form urethanes, then get polyurethanes.[47] Different ratio of isocyanate functionalities to hydroxyl groups in lignin will affect both physical and thermal properties of materials. Glass transition temperature (T_g) will decrease if the isocyanate functionalities to hydroxyl groups is higher.[47] Some researchers showed that tensile properties could be affected by the different ratio of isocyanate functionalities to hydroxyl groups.[74] Other researchers found that the lignin content is another important factor, which could influent the materials properties.[82] Scientists can also make polyurethanes by using xylaric acid-based triisocyanate reacts with lignin.[72] For polyesters synthesis, variety of molecular weight polyesters can be made.[77,79] The thermal property of the polyesters can be affected by the different types of linker , used "flexible" linker resulted for low T_g, and the "stiff" linker resulted for high T_g.[76] The ratio of lignin to other reactants in the polyesters synthesis can also affect the physical properties of

the final polymer product.[81] There are other researches showed that by replacing the hydroxyl groups in the lignin to other functionalized groups, functionalized lignin can also act as a macromonomer in the polymer synthesis, such as polyurethanes, epoxide resins, etc.[44]

Considering the complex structure of lignin will bring difficulties in directly polymerization, researchers started with simple monomers that could be derived from lignin, such as vanillin. As a phenolic monomers of pyrolysis lignin, vanillin can be derived in commercial scale.[44,51,54,83] Comparing to carcinogenic styrene, vanillin has relative low toxicity and volatility.[43,48,53] And with the similar structure of styrene, vanillin became a possible choice to substitute styrene in homopolymers and block copolymers synthesis.[43,48,53,54,84] Methacrylate group acts as one of the major functionalization group after modification of monomer, and the common polymerization method is RAFT polymerization.[43,48,53,85] There are also researches on the using acrylate group as functionalization group, synthesized under radical polymerization.[86] For the polymerization of lignin-derived monomer, scientists had focused on only one or few lignin-derived monomer involved in polymerization process. However, there is almost no research on directly polymerization using lignin as starting monomer material. If the polymer materials directly synthesized via lignin could have comparable physical and thermal properties with those traditional polymers, which synthesized by petroleum-based materials. Then the renewable and low-cost properties will make the lignin-based polymer replace the petroleum-based polymer. Therefore, to develop a method that could directly polymerize the lignin to desirable polymer materials will become a new research direction in lignin field.

Even though, directly synthesized thermoplastic materials by lignin is not a possible way for now. The lignin can be acted as plasticizer to improve the thermal properties of

polymer materials or synthesize the thermoplastic materials when mixed with other polymer materials. The thermoplastic synthesized by lignin-based products and polyester has thermal stability that could reach 200˚C.[54] Early in 1997, scientists were able to fabricate thermoplastic material by mixed poly(vinyl acetate) in kraft lignin.[87,88] Modified kraft lignin blended with polyesters for thermoplastic materials has also been studied.[88]

Because lignin structure contains many aromatic rings, lignin has also been studied for synthesis carbon fibers. First lignin-based carbon fiber was produced in 1967 (Nippon Kayaku Co.),[61,89] which was made by lignosulfonate with poly(vinyl alcohol) as plasticizer, and this is only way to make lignin-based carbon fiber on a pilot scale.[90] Additionally, there are increasingly number of researches that based on lignin as the precursor for low-cost carbon fiber synthesis.[54,61] Different types of lignin-derived precursors were reported, such as: steam-exploded lignin,[91] modified exploded lignin,[92] organosolv lignin (acetic acid pulping),[93,94] kraft lignin blended with poly(ethylene oxide), poly(ethylene terephthalate), and polypropylene,[90,95] etc. Moreover, researchers found that the addition of synthetic polymer in kraft lignin can be used to make carbon fiber that has strength close to commercial carbon fiber.[96]

CHAPTER 3. SYNTHESIS OF NANOCOMPOSITE GELS VIA SURFACE-INITIATED BLOCK COPOLYMERS

Introduction

The nanocomposites polymers or the SI_BCPs that used in NC gel were synthesized using Kalluru's methods, which he introduced in his published article: synthesis of exfoliated polymer/layered silicate nanocomposite (PLSNC).[7] The nano-clay (MMT) is the filler of the nanocomposite, and the clay is modified by adding the surfactant on the surface of clay using surface-initiated method. Then norborenen first added to the long surfactant chain via ROMP method, CPE added as second block by using the same polymerization method. Kalluru optimized the reaction conditions of SI_BCP synthesis process, which provide an efficient way to make SI_BCP in different molecular weight and different block fractions. In his article, he tried different reaction conditions, such as, reaction temperatures, the processes of adding monomer, co-catalyst to catalyst ratios, and reaction time of each monomer.[7] After comparing the difference between the target and actual average molecular weight and PDI, he provided the most suitable reaction condition for each monomer's synthesis. When Kalluru was doing the reverse-ion exchange experiments on the SI_BCPs, he found this kind of nanocomposites could form gel when dissolved with THF and sodium chloride. Furthermore, this interesting phenomenon carried out the research that introduced in this thesis. The NC gels synthesis process introduced in this work is relatively easy. Unlike the NC gels preparation methods from other research papers,[24-26,66-70] the polymer chains already attached on the nano-clay. Simply adding the solvent, polymer, and salt can be the NC gel preparation method of this kind of polymer.

In present work, we have developed a polymeric nanocomposite material that can form high viscosity gels in THF solvent. We have observed that the mechanism of gel formation is entirely different from the already known clay-based gel systems. First, the gel formation is not a result of chemical crosslinking, which is the usual case of nanocomposite hydrogel formation to date. Second, the gel formation does not occur in situ during the polymerization, for example as reported by Haraguchi et al. In this work, the nanocomposite polymeric material was synthesized as a thermoplastic and then gel is reversibly formed by mixing it in THF in presence of an ionic salt. The presumptive mechanism for gel formation would be the formation of a network structure between clay, ionic salt and polymer chains. More detailed explanation on this will be given in results and discussion section of this thesis. We believe the type of synthesis route used for making these nanocomposite materials, which gives exfoliated clay structures, forms the prerequisite needed form a mechanically stable gel structure. Polymer nanocomposites are usually synthesized via melt blending, solution blending and in situ polymerization techniques.[38,97] Depending on the type of synthesis route being used, different degrees of inorganic filler dispersion in the polymer matrix is observed. In situ polymerization is the most favored route to achieve highly dispersed (exfoliated) state for nano filler in polymer matrix. We have successfully employed surface initiated ring opening metathesis polymerization (SI-ROMP) technique for growing a diblock copolymer from the surface of MMT clay.[7] In this work, the same synthesis procedure was adopted for poly(ethylidene norbornene-*b*-cyclopentene) and this material was used to form the high viscosity gels. High viscosity gels were formed with very low solids loading of the clay grafted poly(ethylidene norbornene)-b-poly(cyclopentene) (SI_BCP).

The polymeric materials synthesized in this current work are highly hydrophobic. Though hydrophobic materials showing the above characteristics have applications as viscosity modifiers in oils, we think hydrophilic gels have broader impact and wide application range. We believe that by developing water soluble polymers via surface initiated polymerization route will enable us to synthesize high viscosity gels formed via the mechanism as explained above. These water-soluble nanocomposite materials would have applications as thickening materials in hydraulic fracking, and viscosity modifiers at very low polymer loading compared to present alternative materials.

Experimental Details

Materials

5-norbornene-2,3-dicarbonyl dichloride (97%, Sigam-Aldrich), 11-bromo-1-undecanol (98%, Sigam-Aldrich), pyridine (anhydrous, 99.8%, Sigma-Aldrich), triethylamine (99%, Sigma-Aldrich), diethyl ether (contains 1 ppm BHT as inhibitor, anhydrous, 99.7%, Sigma-Aldrich), magnesium sulfate (anhydrous, ReagentPlus, 99.5%, Sigma-Aldrich), ethanol (Sigma-Aldrich), and montmorillonite clay (Cloisite-Na^+, Southern Clay Products Inc.) were used as received. The chemicals mentioned above are used to make 5,6-di(11-(N,N,N trimethylammonium)undecoxycarbonyl)norbornene, which is surfactant for functionalized montmorillonite clay (fMMT). The surfactant and the fMMT synthesis procedures were provided in Kalluru's published article.[7]

5-Ethylidiene-2-norbornene (contains 100-200 ppm BHT as inhibitor, miture of endo and exo, 99%, Sigma-Aldrich), cyclopentene (96%, Sigma-Aldrich), and methylene chloride (HPLC, Fisher Chemical) are monomers and solvent. Each chemical was packed through

silica gel and activated alumina column to remove the inhibitor. Then, used three cycles of freeze-pump-thaw to remove the oxygen in chemicals. All these three chemicals were stored in glovebox to prevent oxygen and moisture contaminations, and were used within one week. Grubbs Catalyst 1st generation (97%, Sigma-Aldrich), tricyclohexylphosphine (Signa-Aldrich), ethyl vinyl ether (contains 0.1% KOH as stabilizer, 99%, Sigma-Aldrich), and methanol (HPLC, Fisher Chemical) were used as received. The chemicals mentioned above are used in the SI_BCPs synthesis.

Tetrahydrofuran (HPLC, Fisher Chemical) and sodium chloride (Crystalline/Certified ACS, Fisher Chemical) were used as received. These two chemicals were used in the NC gels synthesis.

SI_BCP synthesis

Kalluru's published article stated about different reaction conditions for poly(norbornene), poly(cyclopentene), and poly(norbornene)-b-poly(cyclopentene) synthesis. Therefore, according to his article, in order to achieve the target molecular weight and low PDI. The suggested reaction conditions for first block poly(norbornene) synthesis were 20˚C reaction temperature, semibatch adding process, 1 hour reaction time, and with 4 co-catalyst to catalyst ratio. And the suggested reaction conditions for second block poly(cyclopentene) synthesis were 25˚C reaction temperature, semibatch adding process, 5 hours reaction time, and with 4 co-catalyst to catalyst ratio. The reaction conditions for SI_BCPs with smaller molecular weight have a little bit difference, especially for the SI_BCPs under 80 kDa average molecular weight. The co-catalyst to catalyst ratio changed to 6, the reaction temperature of second block poly(cyclopentene) increased to 30˚C, and the reaction time

extended to 7.5 hours. The first block synthesis used ENbn as monomer, unlike the work done by Kalluru, he used norbornene as first monomer. By applied the same reaction conditions on poly(ENbn) synthesis, the target molecular weight and low PDI can be achieved. The SI_BCPs synthesized for this work have average molecular weight from 50 kDa to 160 kDa, with different ENbn fraction from 0.25 to 0.8.

Gel tests

For preparing the gel tests, 35 mL THF was added into the 40 mL vial with different amounts of SI_BCP and different amounts of sodium chloride (NaCl). Also, a small stirring bar was put into the vial and stirred at 1200 rpm during the whole process. Typically, for general gel tests: 1 w/v% of SI_BCP to THF ratio with 15 wt% (polymer based) NaCl were tested. To find the salt concentration effect and polymer concentration effect on different NC gels, different gel tests have been done in this work. The detail information of the gel tests is provided in Table 3.1, and Table 3.2. Additionally, discovering the gel formation process or gel formation mechanism is also necessary. Therefore, the gel kinetic study was also being done on different NC gels.

Table 3.1 Gel tests detail of different polymer concentrations

[a]Polymer concentration (w/v %)	[b]NaCl concentration (wt %)	[c]THF (mL)
0.1	15	35
0.25	15	35
0.5	15	35
0.75	15	35
1	15	35
1.5	15	35
2	15	35
3	15	35

[a] Polymer concentration indicates percentage of the weight of SI_BCP (gram) to volume of THF (mL) ratio of each gel test.

[b] NaCl concentration indicates the weight percentage of NaCl used in gel each test, that weight percentage is based on the amount of SI_BCP used in gel test.

[c] THF indicates the volume of THF used each gel test.

Table 3.2 Gel tests detail of different NaCl concentrations

[a]Polymer concentration (w/v %)	[b]NaCl concentration (wt %)	[c]THF (mL)
1	5	35
1	10	35
1	15	35
1	20	35
1	30	35
1	50	35
1	70	35
1	100	35
1.5	15	35
1.5	50	35
1.5	70	35
1.5	100	35

[a] Polymer concentration indicates percentage of the weight of SI_BCP (gram) to volume of THF (mL) ratio of each gel test.

[b] NaCl concentration indicates the weight percentage of NaCl used in gel each test, that weight percentage is based on the amount of SI_BCP used in gel test.

[c] THF indicates the volume of THF used each gel test.

Characterization methods

Nuclear Magnetic Resonance (NMR) Spectroscopy NMR was used for analyzing chemical structure of the surfactant. The synthesized surfactant was dissolved in chloroform-D with 0.1% TMS. The NMR spectroscopy recorded with a Bruker Avance III spectrometer (600 MHz), and results were analyzed by MestReNova.

Thermogravimetric Analysis (TGA) Thermal degradation data for fMMT was obtained by thermogravimetric analyzer (TA Instruments). fMMT was heated from room temperature to 900˚C, at 10˚C/min heating rate, and under continuous 20 mL/min nitrogen flow.

Gel Permeation Chromatography (GPC) Molecular weights of SI_BCPs were analyzed by Waters ACQUITY Advanced Polymer Chromatography (APC) System using THF as the eluent, with the flow rate set to 1 mL/min. Data were obtained from RI (Refractive Index) detector in the system. Samples were put into the vacuum oven to dry overnight prior to analysis. Then samples were dissolved in HPLC THF at 1 mg/mL ratio, and passed through the 0.45 mm PTFE filter.

Rheology For viscosity data measurement, Advanced Peltier System (APS) attachment of ARES-G2 with cup and recessed bob geometry were used. Also, a water-cooled chiller was used for temperature control of the experiments. Approximately 10 mL of the NC gel was used in each viscosity measurement, each viscosity test was conducted at 20˚C with shear rate from 100 1/s to 0.01 1/s.

Results and Discussion

Gel mechanism

The NC gels were formed with SI_BCP material with sodium chloride salt and THF. When a nanocomposite is dissolved in THF solvent, polymer chains get solvated and dissolve in the solvent but the clay cannot dissolve in the solvent. However, when sodium chloride is added to this solution, the cations will exchange onto the surface of clay replacing the polymer chain which were attached to clay surface via an alkyl ammonium surfactant.

Thus, the polymeric chains are much more liberated and free to move in the THF solution. For a certain block composition and molecular weight of the diblock in a nanocomposite, the presence of clay, addition of ionic salt, and the polymer chain with alkyl ammonium surfactant head all are held together via interaction forces resulting in a high viscosity nanocomposite gel. A pictorial representation of this mechanism in presented in the Figure 3.1. This representation is just a presumption, we are awaiting more information to ascertain the exact mechanism. In order to further understand the effects of polymer and salt loading on NC gel formation, we have prepared few NC gel samples by varying polymer loading and sodium chloride loading to conduct rheological measurements as reported in the results section below.

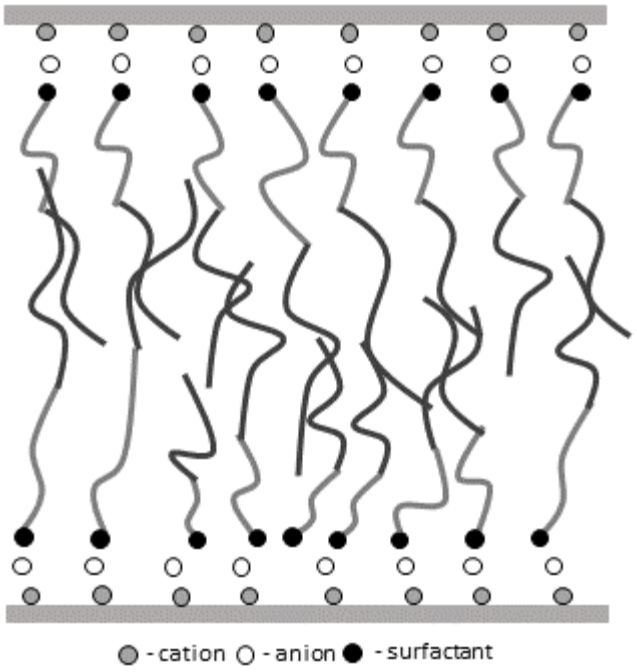

Figure 3.1 The mechanism of the gel formation. The MMT clays (thin gray rectangles) are exchanged with cations (in this case sodium ions) which are ionically bonded to anions (in this case chloride ions) which in turn are attracted to the cationic alkyl ammonium head of the di-block copolymer (poly(ethylidene norbornene)-b-poly(cyclopentene)). Please note that the block lengths are not to scale.

As mentioned before, certain block composition and molecular weight could be one factor that affect the gel formation. The Figure 3.2 summarizes the gel test results on different SI_BCP molecular weights with different di-block composition. Each SI-BCP was tested on 1 w/v% of SI_BCP to THF ratio, with 15 wt% NaCl (polymer based). In the range from 105 kDa to 160 kDa MW, the gel formed when ENbn weight fractions were between 0.5 to 0.65. Other than that range, low or high ENbn weight fraction will not cause the SI-BCPs form gel. In the range from 40 kDa to 100 kDa MW, no gel formation with the ENbn weight fraction range from 0.3 to 0.75. Therefore, the gel only formed at certain ENbn weight fraction range and certain di-block molecular weight.

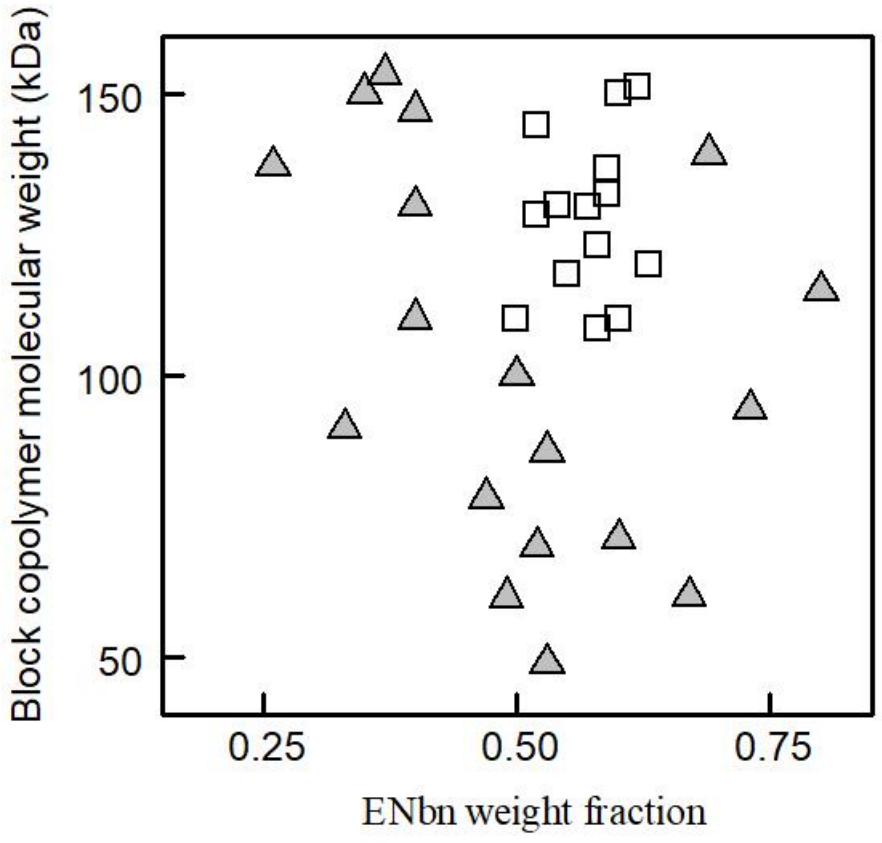

Figure 3.2 Gel phase graph. The grey triangles indicate the SI_BCPs did not form gel. The hollow rectangles indicate the SI_BCPs that formed gel.

Rheology measurements

Next set of graphs show the effects of changing the polymer and salt loading on viscosity of NC gels. The zero-shear viscosity in the following figures refer to the viscosity data at shear rate equals 1 1/s, the viscosity graphs for variety share rate has provided in the Appendix section. Figure 3.3 shows that the influence of polymer concentration on different NC gels. From Figure 3.3, the viscosity increases as the polymer concentration increases for both NC gels. However, the influence of the polymer concentration on different NC gels is not the same. The NC gel with 150 kDa and 62% ENbn is less polymer concentration dependent. Ignoring the bottom two points of the NC gels, the other four points less likely with increasing trend, more likely as scatter plot. Otherwise, the NC gel with 110 kDa and 62% ENbn behaves as polymer concentration dependent. Because, all the points are followed by an increasing trend, which indicated by the dark gray curve showing in the graph. Therefore, for the polymer concentration dependent NC gels, the increasing polymer concentration will cause more polymer chains in NC gel network. The higher amount of polymer chains the easier of the polymer chains interact with others. For the polymer concentration independent NC gels, there are already saturated amount of the polymer chains in the NC gel network structure, the increasing amount of polymer chain will not have too much influence on the NC gel structure.

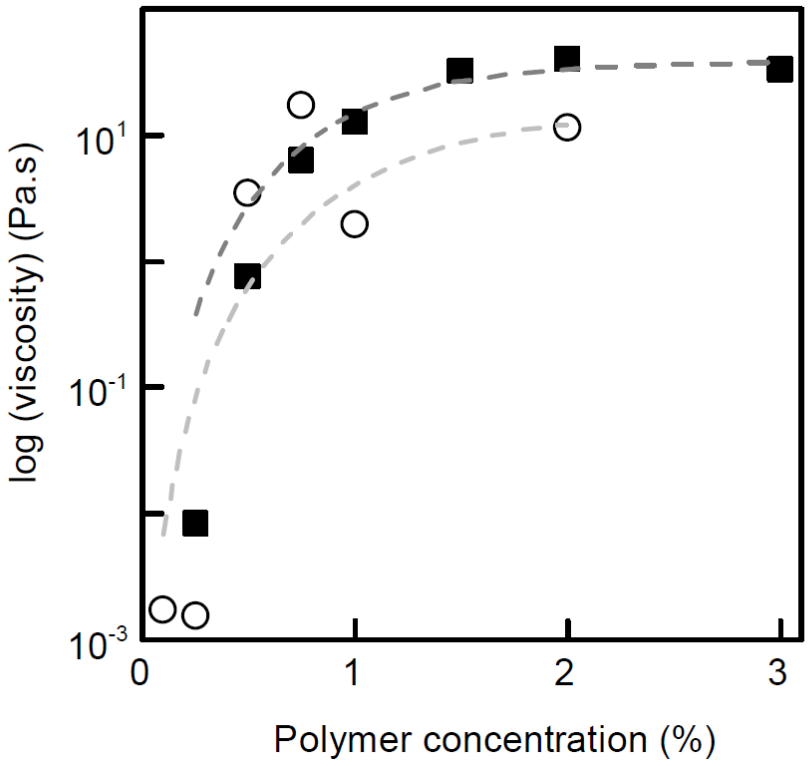

Figure 3.3 Cup and bob measurement of nanocomposite gels formed with different polymer to THF ratio and 15 wt% salt (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction (solid squares) and 150 kDa with 62% ENbn fraction (hollow circles).

Figure 3.4 shows the viscosity profile of 1~w/v\% and 1.5~w/v\% NC gels with variety salt concentrations. For NC gels that formed with nanocomposite that has 110 kDa molecular weight and 50% ENbn, based on 1 w/v% polymer loading and 1.5 w/v% polymer loading, increasing the salt concentration does not show any significant increase in the gel viscosity. The NC gel that formed with nanocomposite that has 150 kDa molecular weight and 62% ENbn, the 1 w/v% polymer loading shows increasing in viscosity when the salt concentration increased. As showed n Figure 3.4, the NC gels that prepared with 110 kDa and 50% ENbn nanocomposite are salt concentration independent, the plots of the increasing in salt concentration is more likely of linear fit. The NC gel prepared with 150 kDa and 62% ENbn is salt concentration dependent, the viscosity increasing as curve fit in the Figure 3.4.

The NC gels that formed by different nanocomposites will have different network structures. The salt independent NC gels already have enough ionic interaction in the network structure. Therefore, the addition amount of the salt will not affect the viscosity of the NC gels. For the salt dependent NC gels do not have enough ionic interaction in the network structure, the more salt adding to the system, the more ionic interactions the polymer chains will have with the metal ionic atoms. However, the increasing of the viscosity will be reached the limitation when the ionic interactions are saturated in the gel network structure. As indicated in Figure 3.4, the higher salt concentration the less increasing of the viscosity, and there will be no increasing in viscosity after the salt concentration is saturated in the NC gels. When certain polymer loading NC gel is prepared with certain salt concentration, increasing the polymer loading may need comparable increase in salt concentration to form a gel with similar viscosity profile. The viscosity plots for 1 w/v% polymer loaded with 15 wt%, 50 wt%, 70 wt%, and 100 wt% lie below the viscosity plots for 1.5 w/v% with all four salt concentrations. Based on this, increasing the polymer concentration may have higher effect on viscosity compared to salt concentration.

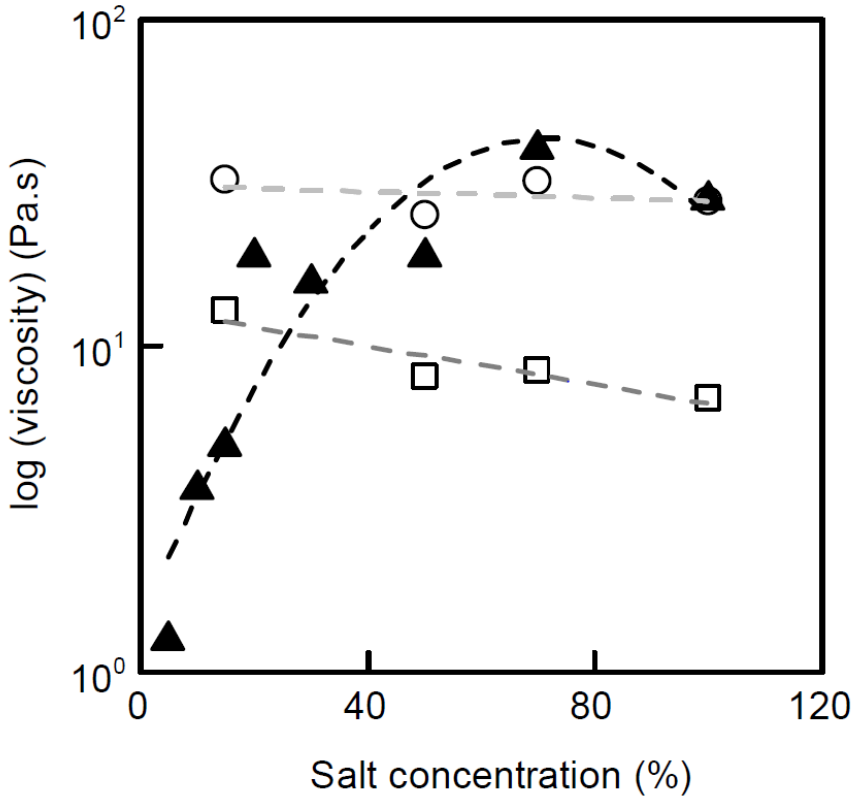

Figure 3.4 Cup and bob measurement of nanocomposite gels formed with 1 w/v% of polymer and different salt concentration (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction (hollow squares) and 150 kDa with 62% ENbn fraction (solid triangles). Nanocomposite gels formed with 1.5 w/v% of polymer and different salt concentration (polymer weight basis), nanocomposite:110 kDa with 50% ENbn fraction (hollow circles).

Figure 3.5 shows the relationship between viscosity profile and the time of stirring of 1 w/v% with 15 wt% salt concentration for two type NC gels. Both NC gels behave the same, at the first few days of stirring, the viscosity does not have too much difference. After certain amount of stirring time, the viscosity starts increasing, which indicating the gel network structure start forming. During the gel formation period, the viscosity increases dramatically in the beginning half to one day, then the rate of viscosity increase slows down, but the viscosity keeps increases as the stirring time goes. After few more days of stirring, the viscosity will have very little increases or remain stable. The gel formation process occurs in

a certain period. When beginning with the stirring, the viscosity will not change too much. After the polymer chains start to interact with the clay, the sodium ionic atoms, and other polymer chains, there will be huge increasing of viscosity in short period. Then the viscosity keeps increasing until the gel network structure completely formed. During this later period, the rate of increasing the viscosity becomes slow. That may because of the most of the polymer chains had already interacted with other polymer chains to form a network structure. But, there will be still some free polymer chains in the system interact with the gel network structure to make the viscosity increased. Until the saturated of the gel network structure or no more polymer chain can be involved in the gel network structure, there will be no increase of viscosity.

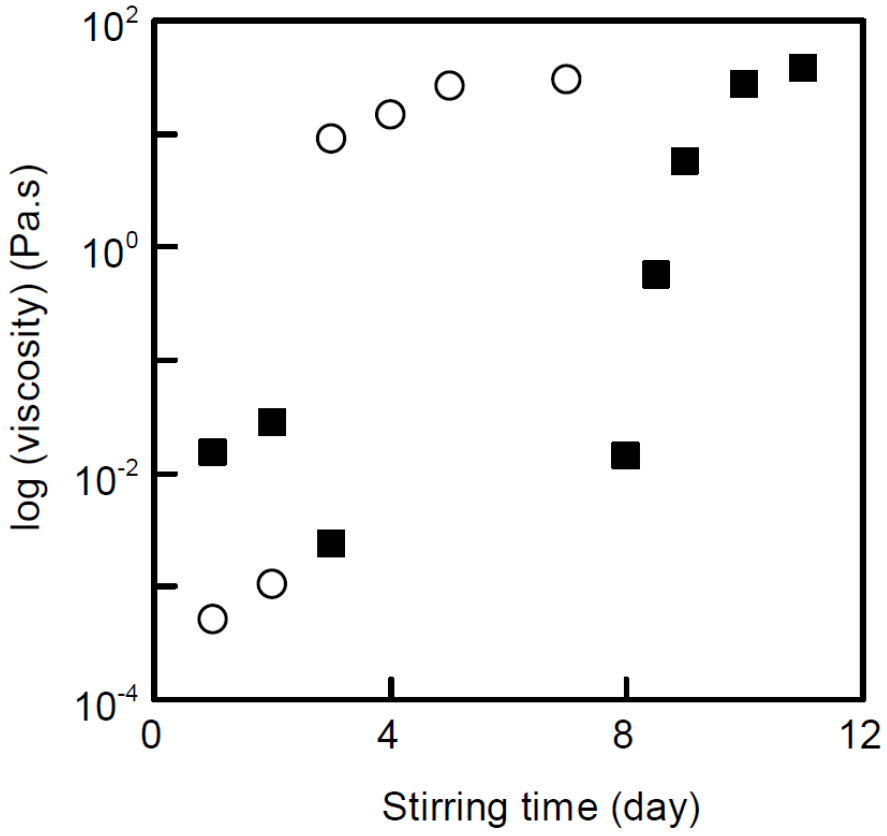

Figure 3.5 Cup and bob measurement of nanocomposite gels formed with 1 w/v% of polymer and 15 wt% salt (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction (solid squares) and 150 kDa with 62% ENbn fraction (hollow circles).

CHAPTER 4. SYNTHESIS OF LIGNIN-BASED POLYMERS DIRECTILY FROM PYROLYSIS LIGNIN VIA RAFT POLYMERIZATION

Introduction

As an amorphous polymer, lignin's complex structure and diverse properties make it hard to do in controlled polymerization without any modification or functionalization. Therefore, scientists started controlled polymerization on fewer compounds mixture, then derived block copolymer. The major controlled polymerization method applied in this field is reversible RAFT polymerization. Because the vanillin can be derived on commercial scale from lignin.[44] Vanillin-derived compounds are important components in the starting materials of RAFT polymerization. Polymerization need double bonds, replacing the plenty hydroxyl groups by other functionalized groups is the first thing need to be considered before polymerization process. Recent years, researchers used methacrylate group to replace hydroxyl group of lignin-derived precursors for RAFT polymerization.[43,55,56,85,98] The results showed the block copolymers have decent thermal stability and viscoelastic properties. However, the researches mentioned above only used limited number of lignin-derived compounds in the precursors. As the number of lignin-derived compounds increases in the precursor, the harder to controlled the polymerization process. Also, CTA for the RAFT polymerization is another challenging part in this area. For this research direction, the functionalized groups could be different. Methacrylate group has been studied most for RAFT polymerization of lignin-derived compounds. Acrylate group could be another possible choice, the similar chemical structure but smaller size than the methacrylate group. Many other functionalized groups with single double bond could all be considered in this research area.

The structure of carbon fiber is sheets of hexagonal pattern that arranged by carbon atoms. As showed in Figure 1.3, lignin has the network structure with benzyl rings attach to different functionalized groups. Therefore, under the certain conditions, it's possible that the benzyl rings in lignin attach together to form hexagonal pattern structure. And the plenty of hydroxyl groups in lignin can be replace by other functional groups. After the modification process, the functionalized lignin could act as carbon fiber precursors. In nowadays carbon fiber's industry, polyacrylonitrile is the main material to make carbon fibers.[99] The used of petroleum-based materials to make carbon fibers still has high cost, which also limit the application field of carbon fibers. Carbon fibers are now used in automotive industry, aerospace industry, etc. If the cost of making carbon fibers can be decreased to acceptable range, other industries also use this material, such as: construction industry, mechanical industry, etc.[99,100] To lower the cost of carbon fibers synthesis, the choice of raw materials should have lower cost and the cost of processing should be lower. Lignin is one of the low-cost material that could make carbon fibers. There are few advantages of using lignin as carbon fibers precursors, such as: low cost, high carbon content, second abundant polymer in nature, high yield after carbonization process, and no toxic product in carbonization process.[100] Many researchers showed that they can derive carbon fibers from lignin. Moreover, Naskar already made the lignin-based carbon fibers that could achieve 1.07 GPa (155 ksi; 109 kg-f/mm^2) average strength and 82.7 GPa (12 Msi; 8440 kg-f/mm^2)moduli, more importantly this carbon fibers has lower cost.[99] The common process for making low-cost carbon fibers from lignin has three major processes if started with carbon fiber precursors: fiber extrusion, stabilization (oxidation), and carbonization.[101] For the fiber extrusion process, the precursors should have low soften temperature. And for the

stabilization process, it requires the precursor to have enough high T_g, which could survive under the heating process. The acceptable T_g range of the precursor is between 130 ˚C to 150˚C, below this range, the heating rate for oxidation during the stabilization process will be very small, and it will take very long time for this process. Above this range, the precursors become hard to be extruded to fiber.[99] The molecular weight and the linearity of the precursors will affect the T_g, the precursors with linear structure will has lower T_g than the precursors that have the same molecular weight but with the network structure. Generally, higher of the molecular weight the higher of its T_g, and the network structure will also make the T_g higher. Polymerization is way that can make lignin into linear structure. If the final carbon fibers precursor has high molecular weight with the linear structure, it can be easily extruded to fiber under the decomposition temperature of precursor. The precursor with high molecular weight has better thermal stability that can survive through the stabilization and carbonization process, the final carbon fibers might have better mechanical properties. Therefore, use RAFT polymerization to synthesize polymer from pyrolysis lignin is a possible method to make carbon fibers precursors. This kind of precursors can be made to carbon fibers with low-cost property, and have similar mechanical properties compare to the petroleum-based carbon fibers.

Convert lignin to polymeric materials become a very popular research filed recently, because of its renewable and recyclable properties. And most importantly lignin is bio-based material, which will be environmentally friendly, and less harmful to our planet. There are many possibilities for developing polymeric materials from lignin, and for using lignin as raw material to make polymer materials is potential field that scientists and researchers only started in past 10 years. There will be increasing number of new researches on converting

lignin to polymeric materials in the future, and the carbon fibers precursor preparations through RAFT polymerization directly from pyrolysis lignin in one of the new researches that has not been reported.

Experimental Details

Materials

Methacryloyl chloride (97%, contains about 200 ppm monomethyl ether hydroquinone as stabilizer, Sigma-Aldrich), triethylamine (99%, Sigma-Aldrich), acetyl chloride (99%, Sigma-Aldrich), methylene chloride (99.5%, Fisher Scientific), and 1,4-dioxane (99%, Fisher Scientific) were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Sigma-Aldrich) was recrystallized from methanol and stored in freezer until use. And, pyrolysis lignin was provided by Dr. Xianglan Bai's group.

Monomer synthesis

Pyrolysis lignin was first dissolved in methylene chloride, then filtered out the undissolved part. Lignin methacrylate was prepared by reaction between methacryloyl chloride and pyrolysis lignin that dissolved in methylene chloride, triethylamine was added to react with by-product hydrochloric acid. The reaction time took overnight. After the reaction is completed, deionized water is added to the reaction flask, the undesired product triethylamine hydrochloride will move to aqueous phase. Wash two times with deionized water to remove the triethylamine hydrochloride. To remove the unreacted phenolic compounds and the methacrylic acid in the lignin methacrylate, 1 M and 0.5 M sodium hydroxide aqueous solution were used. To avoid the inhibition during the polymerization,

lignin methacrylate need to go through the acetylation process, the remaining hydroxyl groups were reacted with acetyl chloride convert to acetate groups, the triethylamine was used afterwards to react with hydrochloride. After the acetylation process, deionized water was used to remove triethylamine hydrochloride, and the saturated aqueous sodium bicarbonate solution was used to remove the acetic acid. Finally, the methylene chloride in lignin methacrylate will be removed through the rotary evaporator under the vacuum condition and overnight dry in the vacuum oven.

Chain transfer agent (CTA)

The CTA used for lignin methacrylate polymerization is 2-cyanopropan-2-yl ethyl carbonotrithioate (CYCART), which was used for controlled polymerization of lignin methacrylate.[102]

Polymer synthesis

Poly(lignin methacrylate) was synthesized via RAFT polymerization and free radical polymerization. Functionality 1 of lignin methacrylate was used as monomer, and different molecular weight of polymers were synthesized. For the RAFT polymerization, AIBN used in the reaction was 80% mol/mol ratio of CTA, 1,4-Dioxane as the solvent for the lignin methacrylate polymerization. The reaction conditions for poly(lignin methacrylate) state as following: the mixture of monomer, CTA, and AIBN was purged with argon for 30 mins, and the polymerization proceed in 90˚C oil bath for 4 hours. The only difference of the free radical polymerization is without the CTA. The polymer products were put into vacuum oven overnight to dry out the solvent, then precipitated by methanol.

Thermal treatment

This process is used to prepare the carbon fiber precursor. After dried out in the vacuum overnight the polymer products were heating in 165˚C oil bath for 2 hours with the stirring bar. The purpose of this process is to remove the volatiles in the polymer products, and to increase the thermal stability of the polymer materials. The fiber extrusion process requires the materials behave stable around relative high temperature (around 150˚C), if the materials are not thermal stable during the extruding process, the extruded fiber will be porous and have poor mechanical properties when making to carbon fibers.

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy. Functionality of lignin methacrylate was obtained from 1H NMR spectroscopy recorded in deuterated methylene chloride with a Bruker Avance III spectrometer (600 MHz), and results were analyzed by MestReNova.

Gel Permeation Chromatography (GPC). The molecular weight distribution of poly(lignin methacrylate) was characterized and analyzed by Waters ACQUITY Advanced Polymer Chromatography (APC) System using THF as the eluent, with the flow rate set to 1 mL/min. Data were obtained from RI detector and UV detector in the system. Samples were put into the vacuum oven to dry overnight prior to analysis. Then samples were dissolved in HPLC THF at 1 mg/mL ratio, filtered and sampled. Samples were prepared at 5 mg/mL in THF that contain 0.1 M lithium chloride (LiCl), which LiCl was used to avoid the association

between lignin molecules[103]. Then, the samples were passed through the 0.45 mm PTFE filter.

Differential Scattering Calorimetry (DSC). Glass transition temperatures (T_gs) for each poly(lignin methacrylate) and poly(lignin acrylate) were obtained via differential scanning calorimetry (DSC, TA Instrument Q2000 with refrigerated cooling system RCS90). Polymer samples were first dried under reduced pressure for 24 hours. 4-6 mg polymer powder was used for T_g measurement. Data were collected under 50 mL/min nitrogen flow with temperature ramps between 0 ˚C to 200˚C, for three heating and cooling cycles. T_gs were determined from the third cycle.

Thermogravimetric Analysis (TGA). Thermal degradation data for each poly(lignin methacrylate) was obtained by using a Mettler Toledo TGA/DSC instrument. Polymer samples were heated at rate of 10˚C/min from 25˚C to 1000˚C under continuous 100 mL/min nitrogen flow, then samples were heated at constant temperature of 1000 ˚C for 30 minutes under 100 mL/min air flow.[63]

Gas Chromatography Mass Spectrometry (GC/MS). An Agilent 7890B gas chromatography (GC) with Agilent 5977A mass-selective-detector (MSD) and flame ionization detector (FID) system was used to identify the chemical composition in the pyrolytic lignin. The capillary column used in the GC was a ZB-1701 (60 µm×250 µm×0.25 µm). The injection temperature was 250˚C and the oven temperature was kept at 40˚C for 3 min, and then ramped to 280˚C with 3˚C/min.[63]

Results and Discussion

Components in pyrolysis lignin

As mentioned in Qu's published paper, through the GC/MS results, as showed in Figure 1.4 the pyrolysis lignin used in this work has following phenolic monomer components: syringol, 3',5'-dimethoxyacetophenone, 1,2,4-trimethoxybenzene, etc. Also, this pyrolysis lignin includes some carbohydrate derived components, such as: levoglucosan, 1,2-cyclopentanedione, etc.[63]

Poly(Lignin Methacrylate)

After the RAFT polymerization, the reaction vial was first dried in the vacuum oven overnight to remove the solvent, then precipitated by methanol. For different functionalities of poly(lignin methacrylate), different molecular weights of polymer were synthesized.

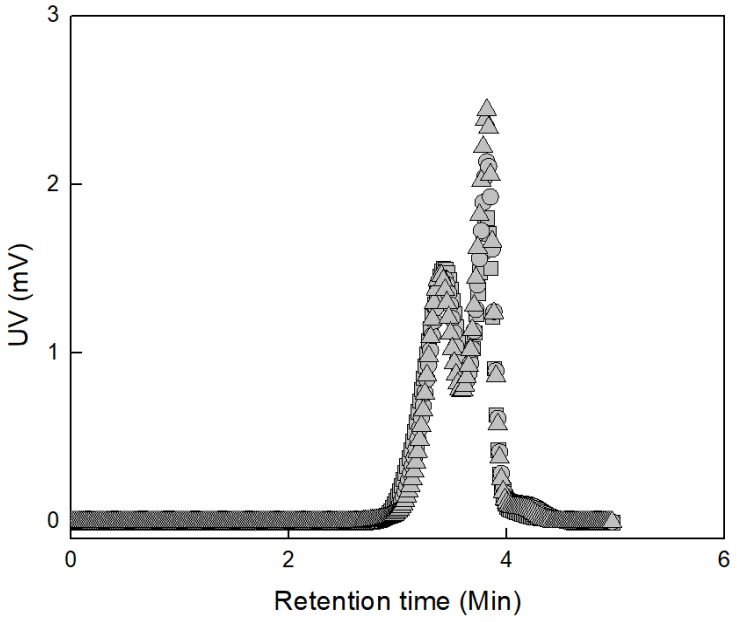

Figure 4.1 GPC results of 1.5 functionality poly(lignin methacrylate) target 20 kDa (solid squares), 100 kDa (solid circles), and 300 kDa (solid triangles). The lignin methacrylate that used for polymerization was not washed by sodium hydroxide and not been acetylated.

The Figure 4.1 showing the UV signals from GPC of 1.5 functionality poly(lignin methacrylate), there are two peaks showing in the figure, the first peak is polymer peak of poly(lignin methacrylate), and the second peak is solvent peak of THF. Figure 4.1 shows GPC signals of three different poly(lignin methacrylate), the target molecular weights of poly(lignin methacrylate) are 20 kDa, 100 kDa, and 300 kDa. But, as showed in the figure, the UV signals do not have too much difference for different target polymers. That means the molecular weights do not change too much when the amount of CTA changes during the polymerization process. The chain growth of polymer might inhibit by other phenolic compounds that do not modified by methacrylate group. Therefore, the unreacted phenolic compounds need to be removed in the lignin methacrylate before the polymerization process.

Figure 4.2 shows the GPC traces of poly(lignin methacrylate) that before and after the acetylation process of the lignin methacrylate. The red solid line shows the GPC trace of poly(lignin methacrylate) that target for 50 kDa, with the acetylation of the monomer, and the black solid line shows the GPC trace of poly(lignin methacrylate) that target for 100 kDa without the acetylation of the monomer. The molecular weight has increased after the acetylation of monomer, which means the monomer used for the polymerization without acetylation has some hydroxyl groups that inhibited the polymerization process. Therefore, even target for the high molecular weight, the hydroxyl groups inhibited the polymer chains to grow in the polymerization, and resulted in the low molecular weight of poly(lignin methacrylate). After the acetylation process of monomer, most of the hydroxyl groups converted to the acetate groups, the polymer chains growth will not inhibit by the hydroxyl groups. Which the molecular weight has been increased through the polymerization process.

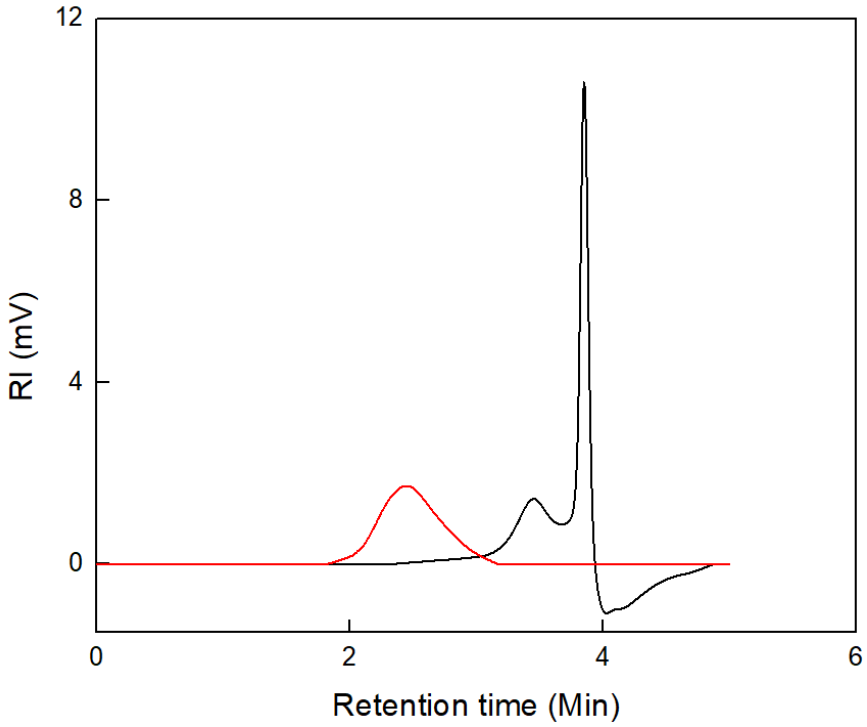

Figure 4.2 GPC results of 1 functionality poly(lignin methacrylate) that target 100 kDa before the acetylation of monomer (black solid line), and target 50 kDa after the acetylation of monomer (red solid line).

The Table 4.1 is showing the different polymerization method, number average molecular weight, weight average molecular weight, PDI, and conversion of different molecular weight poly(lignin methacrylate).

Table 4.1 Detail information of different molecular weights poly(lignin methacrylate)

[a]Material name	Polymerization method	[b]M_n (kDa)	[b]M_w (kDa)	PDI	Conversion (%)	T_g (°C)
PLM_1	RAFT	51.65	73.20	1.41	71.25	97.31
PLM_2	RAFT	54.17	71.12	1.31	49.72	109.33
PLM_3	RAFT	84.31	161.11	1.91	30.07	111.62
PLM_4	Free radical	33.85	60.73	1.79	69.17	111.32

[a] PLM represents poly(lignin methacrylate), functionality 1 lignin methacrylate used in the polymerization process.

[b] Number average molecular weight.

[c] Weight average molecular weight.

The controlled RAFT polymerization resulted in the smaller PDI than the free radical polymerization, as the number average molecular weight of poly(lignin methacrylate) increases the conversion of the RAFT polymerization decreases. That might cause by the amount of the free radicals, for synthesizing small molecular weight poly(lignin methacrylate) the AIBN amount is larger than for synthesizing large molecular weight poly(lignin methacrylate). Therefore, the amount of the free radical is still a factor that effect the conversion during the polymerization. The higher molecular weight of poly(lignin methacrylate) the more difficult for the polymerization synthesis. Because the higher molecular weight synthesis has less free radical, so the conversion will be low, and it's harder to obtain the target molecular weight. Comparing the T_g through the RAFT polymerization method, the higher molecular weight the larger of the T_g. Comparing the T_g by different polymerization method, the poly(lignin methacrylate) synthesized by free radical polymerization method has higher T_g than the poly(lignin methacrylate) that has similar molecular weight synthesized via RAFT polymerization. To conclude, the RAFT controlled polymerization method could generate poly(lignin methacrylate) with smaller PDI, and smaller T_g than the free radical polymerization.

Figure 4.3 shows the TGA graph of poly(lignin methacrylate) in different polymerization methods and different molecular weight. The temperature was heated up from 25˚C to 1000˚C, and most of poly(lignin methacrylate) was decomposed around 350˚C, finally there is around 20 wt% of the material left after heated up to 1000˚C. The TGA graph does not show too much different between the poly(lignin methacrylate) that varied by molecular weight for RAFT polymerization materials, all these 3 materials behaved almost same when heated from 25˚C to 1000˚C. However, the poly(lignin methacrylate) synthesized

via free radical polymerization has less thermal stability, more materials has been decomposed around 300˚C. Looking through the amount of material left (fixed carbon) after heated up to 1000˚C, although the amount of fixed carbon is different for different poly(lignin methacrylate), they are all in the range from 20 wt% to 25 wt%.

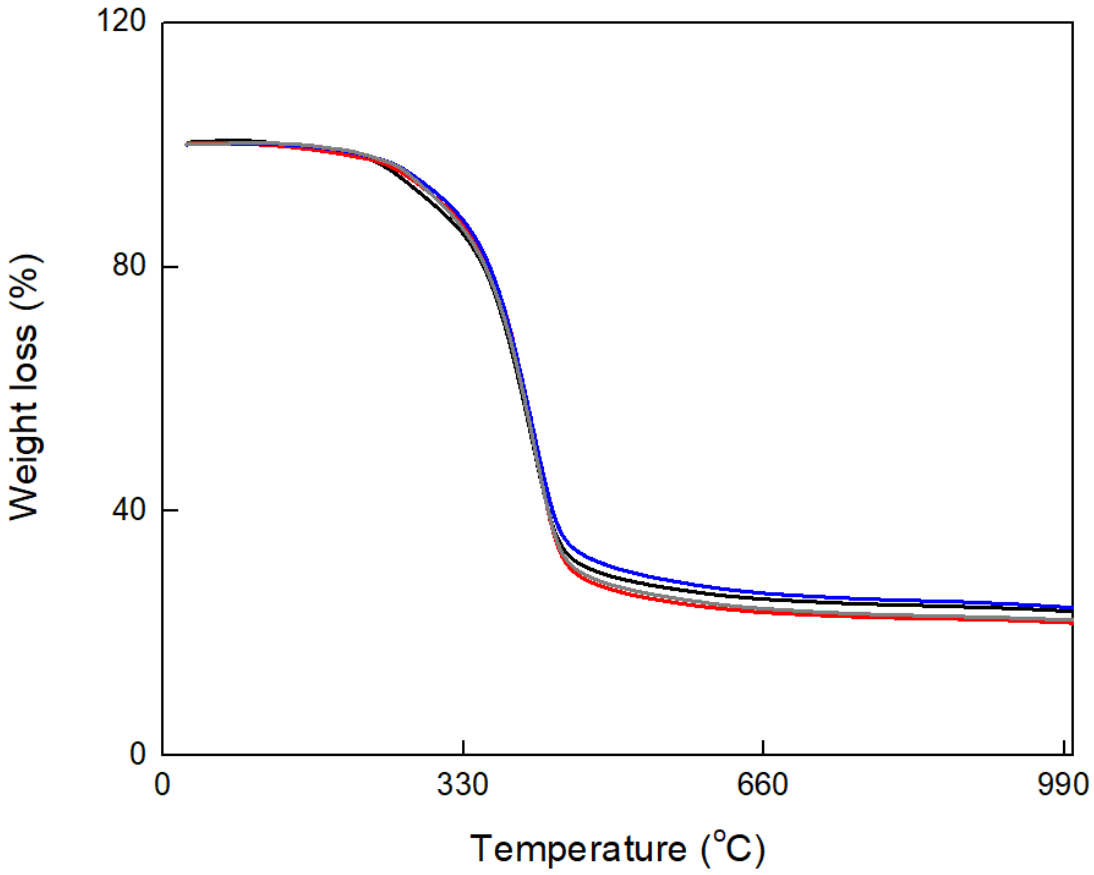

Figure 4.3 TGA data of poly(lignin methacrylate) that has different molecular weight and synthesized by different polymerization methods. PLM_1 (blue solid line), PLM_2 (gray solid line), PLM_3 (red solid line), and PLM_4 (black solid line).

Carbon fiber precursor

The poly(lignin methacrylate) obtained from the precipitation method usually has high T_g, and under the 200°C the polymer is only be soften, not melting. Therefore,

poly(lignin methacrylate) precipitated by methanol is not likely to use for the carbon fiber precursor. Unlike the precipitation method, the thermal treatment method is a devolatilization process that will remove the solvent and some other small molecular weight compounds. During this process, the viscosity of the material increases as the time of stirring increases. Which is because of the volatiles has been removed, the remaining materials is mixture of relative low molecular weight and high molecular weight poly(lignin methacrylate). The Table 4.2 summarizes the molecular weight information and glass transition temperature of one of the poly(lignin methacrylate) that used as carbon fiber precursor.

Table 4.2 Detail information of poly(lignin methacrylate) after thermal treatment for carbon fiber precursor

[a]M_n (kDa)	[b]M_w (kDa)	PDI	T_g (˚C)
3.4	13.1	3.84	88

[a] Number average molecular weight.
[b] Weight average molecular weight.

From the Table 4.2, this poly(lignin methacrylate) has relative high PDI, which means the polymer material contains both high molecular weight and low molecular weight polymer chains. Because the short polymer chains in the mixture will decrease the T_g, the T_g is lower than the poly(lignin methacrylate) if only contains long polymer chains. Additionally, the short polymer chains can also make the materials melting at lower temperature. The polymers that obtained from precipitation method only become soft when increased temperature to 200°C, but the polymer mentioned in Table 4.2 is mostly liquid like at 165°C. As mentioned in the introduction part, the carbon fiber precursor should have low T_g that the precursor will not decompose under the extrusion process. At 200°C the material will decompose, the polymer obtained from precipitation method is not suitable for carbon

fiber synthesis. Otherwise, the polymer after thermal treatment process can be used as carbon fiber precursor.

The glass transition temperature is not the only one requirement for carbon fiber synthesis, there are many other factors, such as the amount of fixed carbon in the material, etc. The amount of fixed carbon is very important factor, which the higher the amount of fixed carbon, the easier for the materials to survive in the stabilization process. The Figure 4.2 shows the TGA graph of poly(lignin methacrylate) that illustrated in Table 4.2. The polymer after thermal treatment is very stable before the temperature reached 200°C, which means under the extruding process, the materials will not decompose, and the extrusion fiber will not be porous. Also after the temperature reached 1000°C, there is still about 25 wt% material left, that means this material contains 25 wt% fixed carbon. To conclude, this material satisfies the requirements of carbon fiber synthesis, which can be used as carbon fiber precursor. The Figure 4.3 shows the fibers after extruding process of poly(lignin methacrylate) that mentioned in Table 4.2.

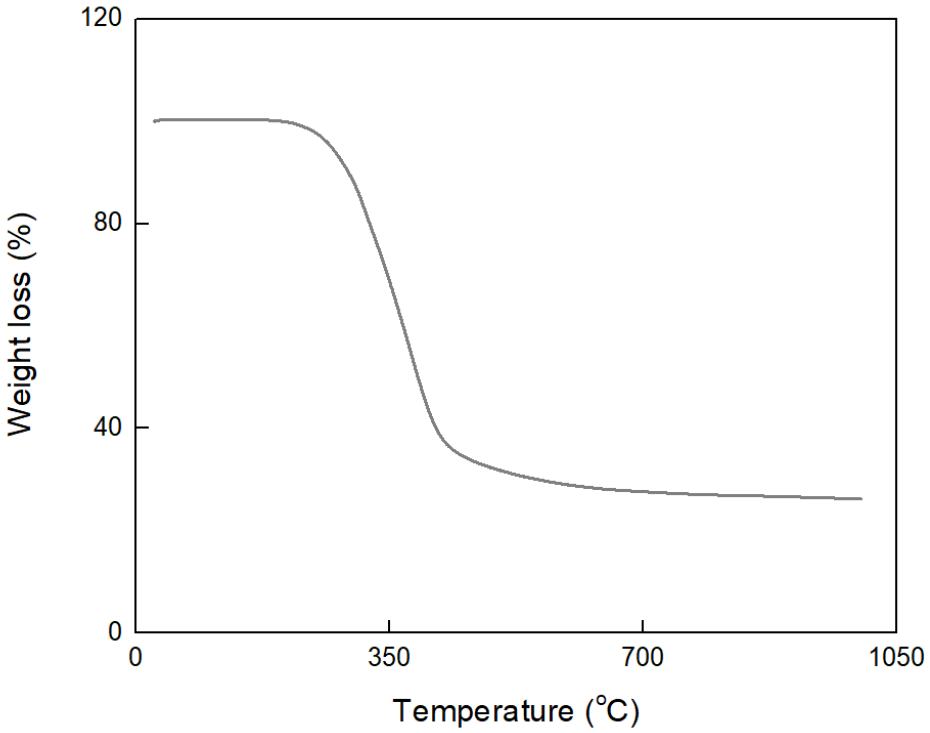

Figure 4.4 TGA graph of poly(lignin methacrylate) after thermal treatment.

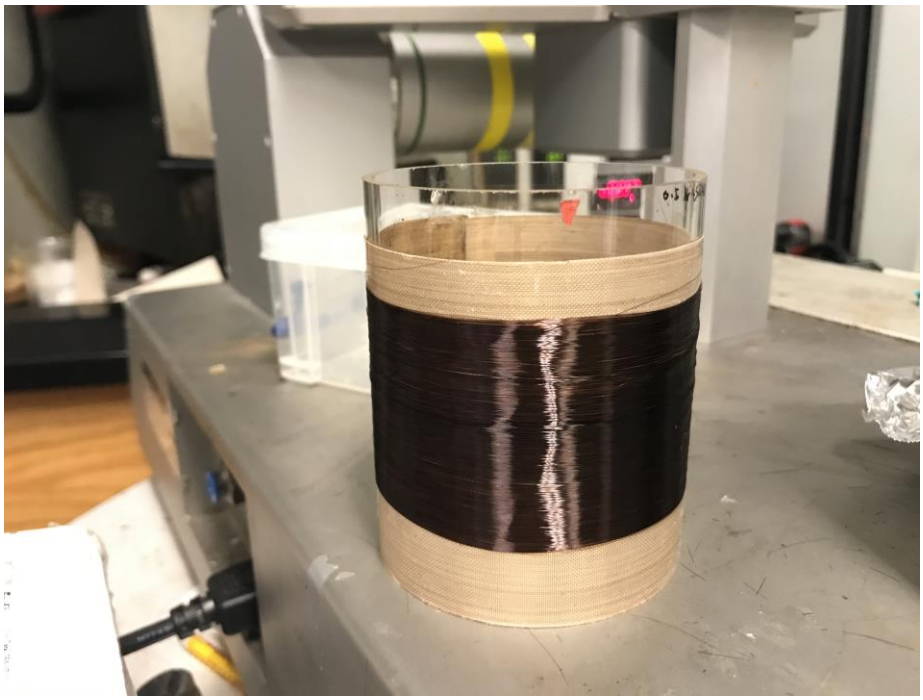

Figure 4.5 Extrusion fibers of poly(lignin methacrylate) after thermal treatment.

CHAPTER 5. SUMMARY AND CONCLUSION

PART – A: Nanocomposite Gel

Block copolymer nanocomposites of poly(ethylidene norbornene-b-cyclopentene) synthesized via surface initiated ROMP when dissolved in tetrahydrofuran solvent along with an sodium chloride results in formation of very high viscosity gels. The polymer chains in the nanocomposite gel formed a “cross-linked” network structure. The nanocomposite gels will be formed only on the block copolymers that with certain molecular weight and ENbn fraction. The formation of high viscosity nanocomposite gel can be divided in three phases. During the first serval stirring days, the viscosity of the THF, sodium chloride, and the block copolymer nanocomposite mixture will not change too much, the viscosity is almost as same as the pure THF. Then during the gel formation process, the viscosity of the mixture will suddenly increasing in half to one stirring day, then formed nanocomposite gel. After the second phase, the viscosity of nanocomposite gel will slowly increase as the time of stirring increases, at some point, the viscosity will reach its maximum and have very little change. The nanocomposite gel formation also varies by the block copolymer concentration, very low block copolymer concentration will not result in forming high viscosity gel. According to the viscosity data of various salt concentration and various block copolymer concentration on different nanocomposite gels. The salt concentration and block copolymer concentration have different effects on different nanocomposite gels.

PART – B: Lignin-based polymers

Pyrolysis lignin is the starting material of this project, after modifying by methacrylate groups, hydroxyl groups replace by methacrylate groups, which methacrylate groups will provide double bonds during the polymerization process to make lignin-based polymer and carbon fiber precursor. Because the remaining hydroxyl groups in the lignin methacrylate will inhibit the polymerization process, acetylation process is used to replace the hydroxyl groups to acetate groups, which can avoid the inhibition of hydroxyl groups during the polymerization. Using lignin methacrylate as monomer, polymers can be synthesized directly through the lignin methacrylate via RAFT and free radical polymerization methods, but by comparing the molecular weight, PDI, polymerization conversion, and other thermal properties, poly(lignin methacrylate) derived from those two methods are different. The free radical polymerization has higher conversion than the RAFT polymerization, but has large PDI and higher T_g. Comparing the different molecular weight of poly(lignin methacrylate) synthesized via RAFT polymerization, the higher molecular weight has higher T_g. The TGA data does not show too much difference between different polymerization method and different molecular weight poly(lignin methacrylate). Using the thermal treatment method, the poly(lignin methacrylate) synthesized in this work can be also provided as the carbon fiber precursor, because of its low T_g, thermal stability during the extrusion process, and has certain amount of fixed carbon.

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APPENDIX. SUPPORTING MATERIALS

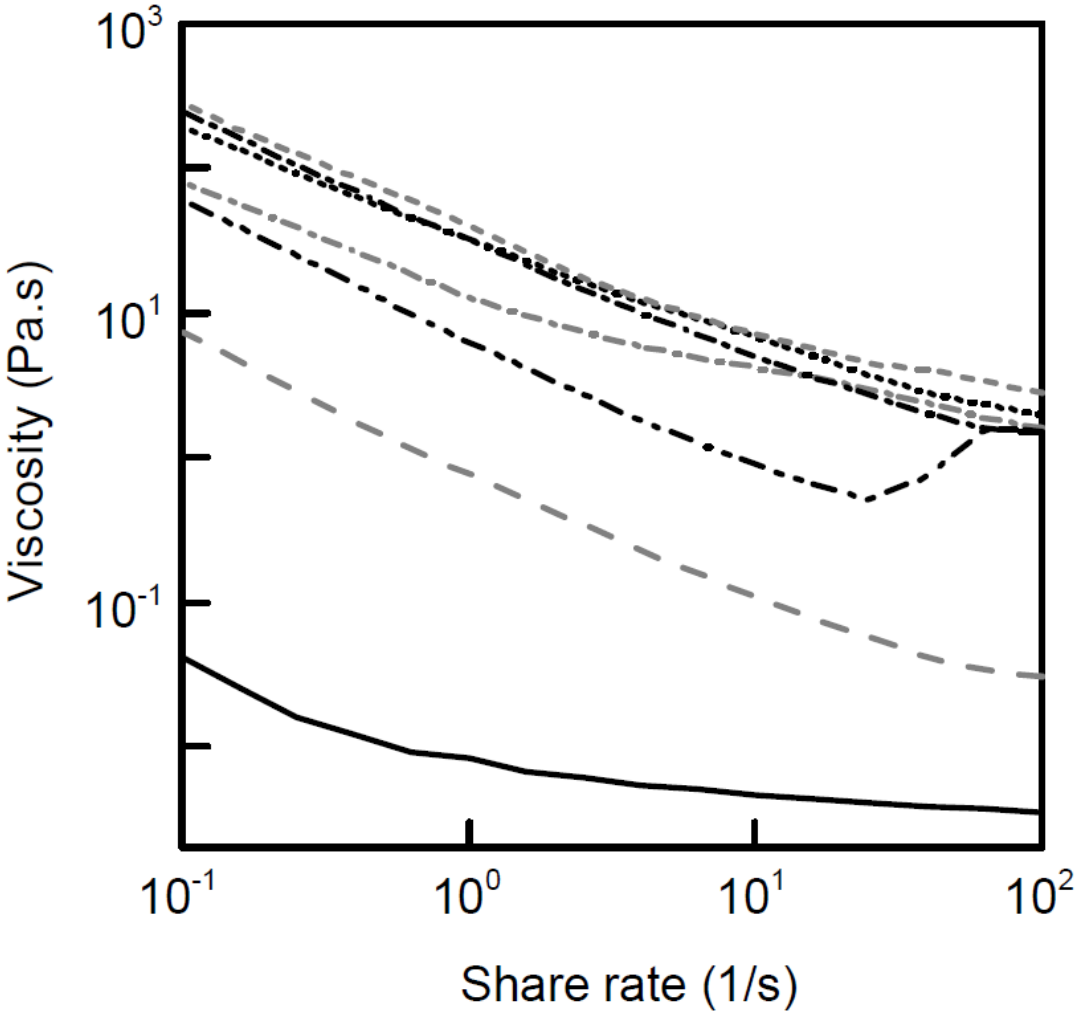

Figure A.1 Cup and bob measurement of nanocomposite gels formed with different polymer to THF ratio and 15 wt% salt (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction. 0.25 w/v% (black solid line), 0.5 w/v% (gray dash line), 0.75 w/v% (black dash dot dot line), 1 w/v% (gray short dash dot line), 1.5 w/v% (black short dot line), 2 w/v% (gray short dash line), and 3 w/v% (black short dash dot line).

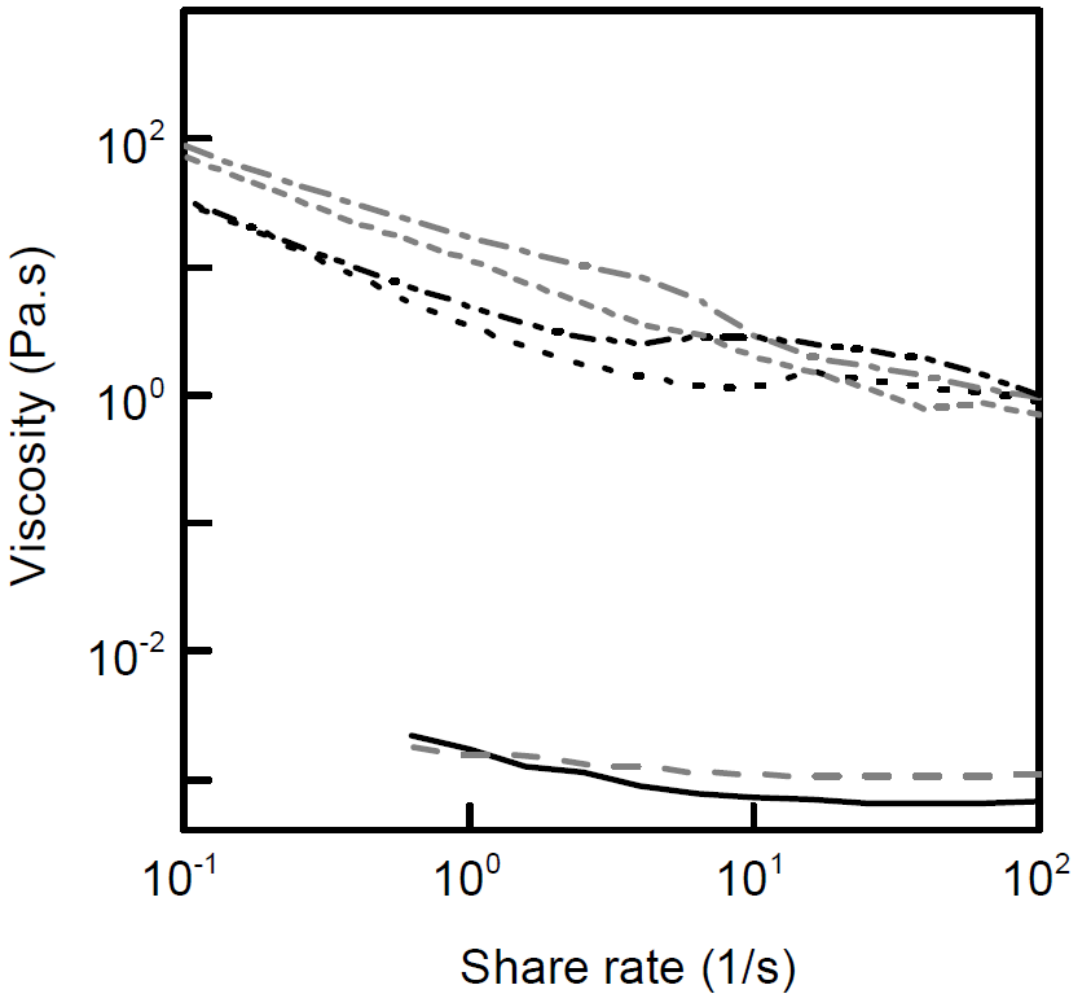

Figure A.2 Cup and bob measurement of nanocomposite gels formed with different polymer to THF ratio and 15 wt% salt (polymer weight basis), nanocomposites:150 kDa with 62% ENbn fraction. 0.1 w/v% (black solid line), 0.25 w/v% (gray dash line), 0.5 w/v% (black dot dot line), 0.75 w/v% (gray dash dot line), 1 w/v% (black dash dot dot line), and 2 w/v% (gray short dash dot line).

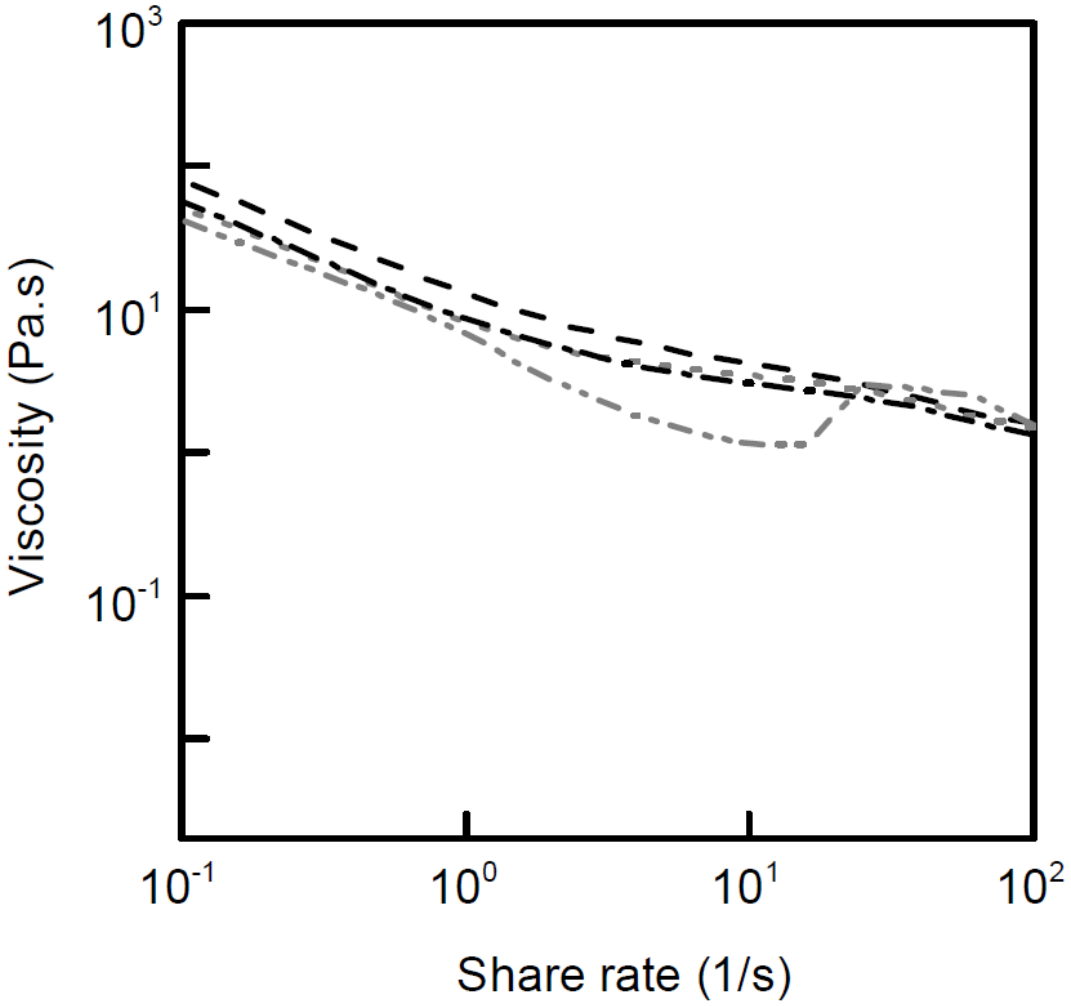

Figure A.3 Cup and bob measurement of nanocomposite gels formed with 1 w/v% polymer concentration and different salt concentration (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction. 15 wt% (black dash line), 50 wt% (gray dot line), 70 wt% (black dash dot line), and 100 wt% (gray dash dot dot line).

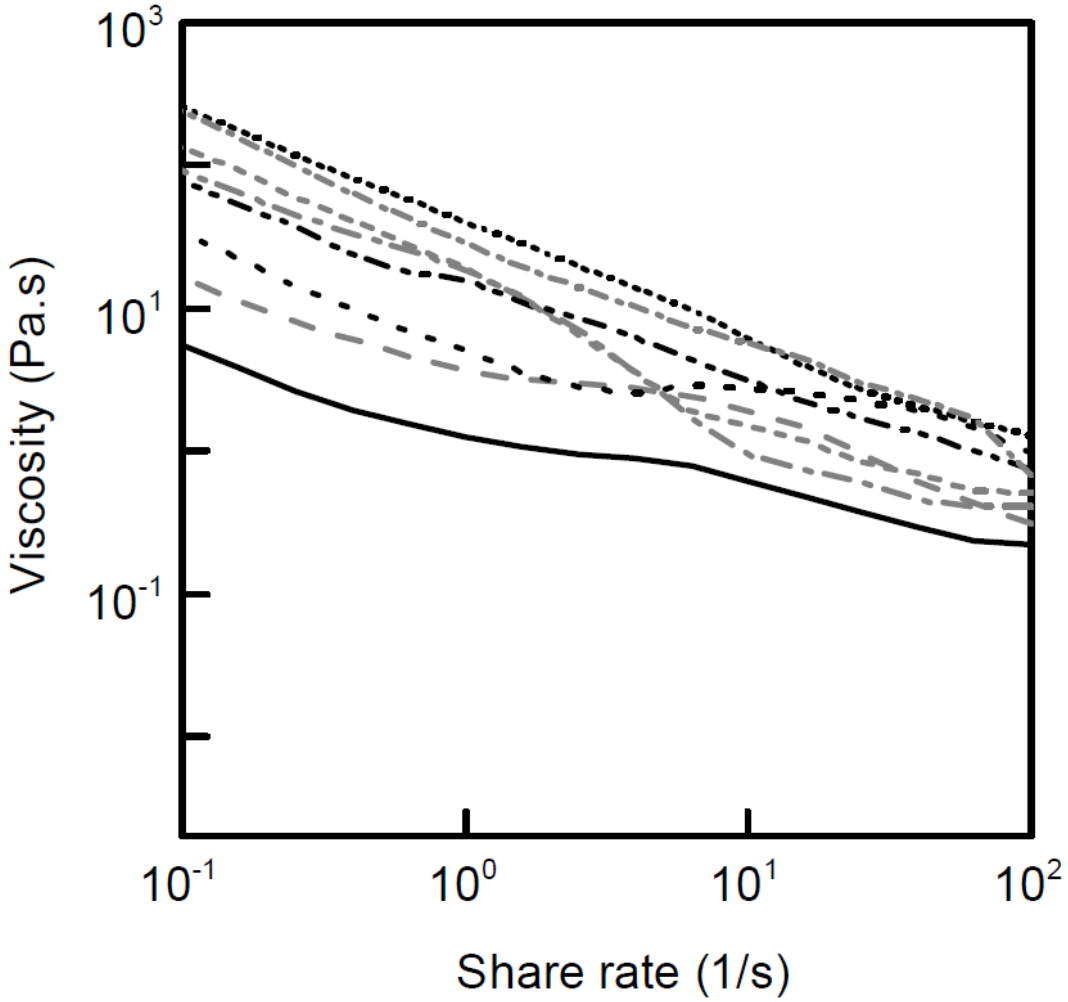

Figure A.4 Cup and bob measurement of nanocomposite gels formed with 1 w/v% polymer concentration and different salt concentration (polymer weight basis), nanocomposites:150 kDa with 62% ENbn fraction. 5 wt% (black solid line), 10 wt% (gray dash line), 15 wt% (black dot line), 20 wt% (gray dash dot line), 30 wt% (black dash dot dot line), 50 wt% (gray short dash line), 70 wt% (black short dot line), and 100 wt% (gray short dash dot line).

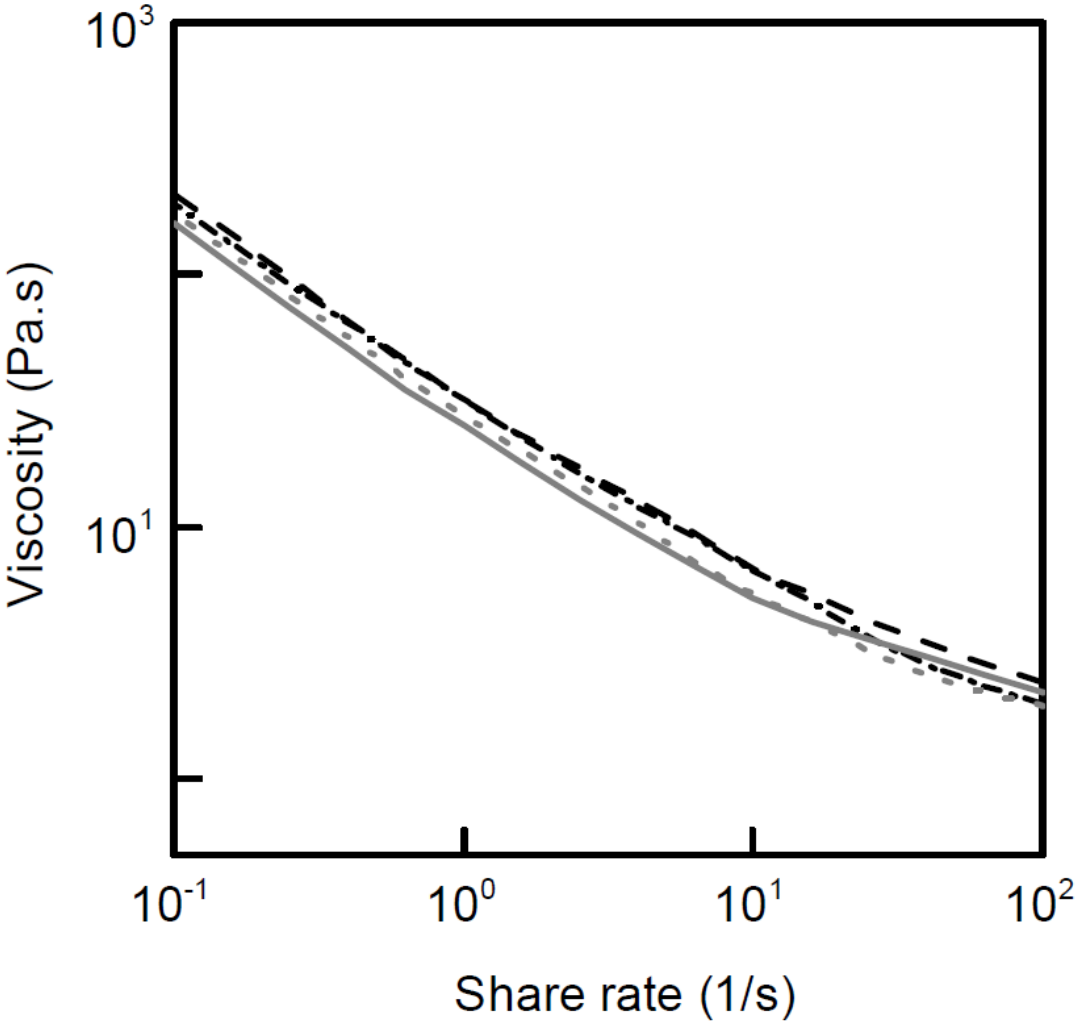

Figure A.5 Cup and bob measurement of nanocomposite gels formed with 1.5 w/v% polymer concentration and different salt concentration (polymer weight basis), nanocomposites:110 kDa with 50% ENbn fraction. 15 wt% (black dot dot dash line), 50 wt% (gray solid line), 70 wt% (black dash line), and 100 wt% (gray short dash line).

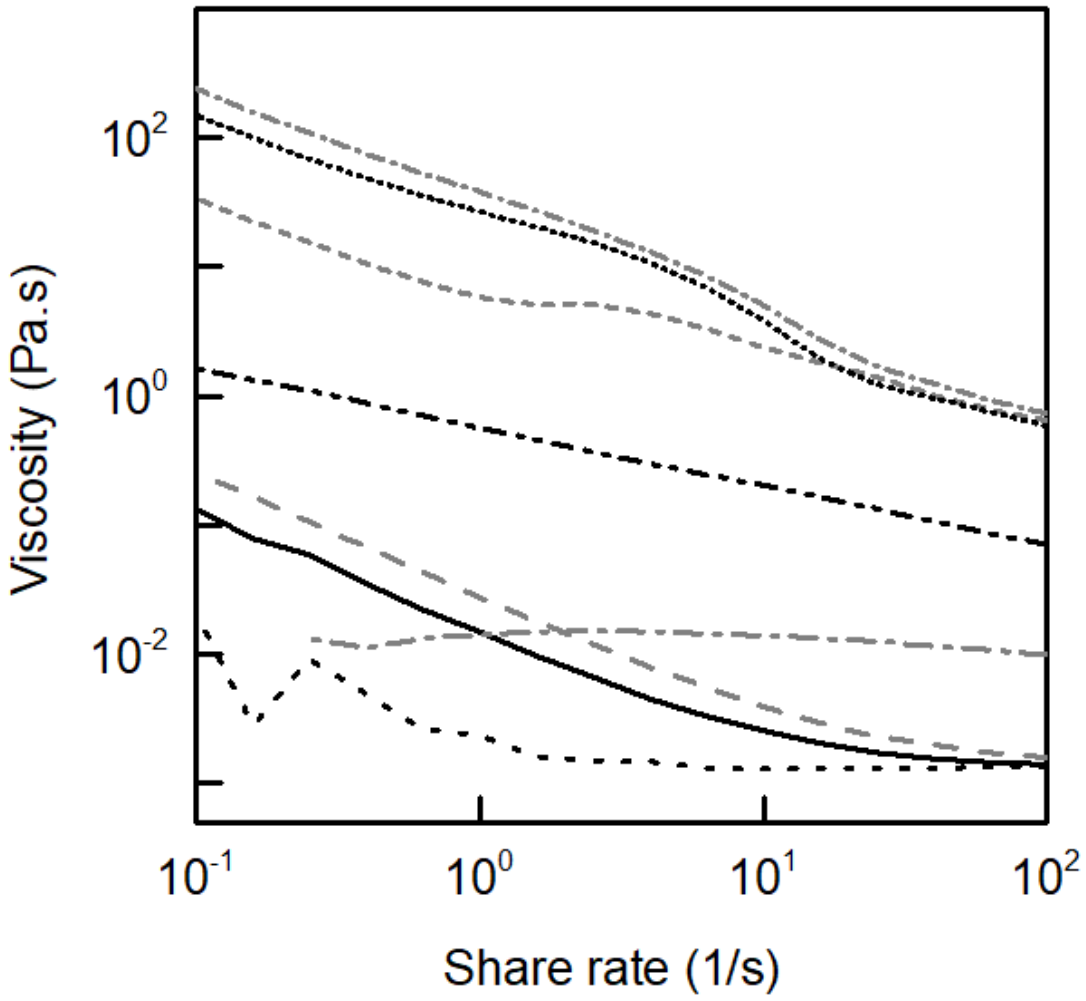

Figure A.6 Cup and bob measurement of nanocomposite gels formed with 1 w/v% of polymer and 15 wt% salt (polymer weight basis), nanocomposites: 110 kDa with 50% ENbn fraction. Day 1 (black solid line), day 2 (gray dash line), day 3 (black dot line), day 8 (gray dash dot line), day 8.5 (black dash dot dot line), day 9 (gray short dash line), day 10 (black short dot line), and day 11 (gray short dash dot line).

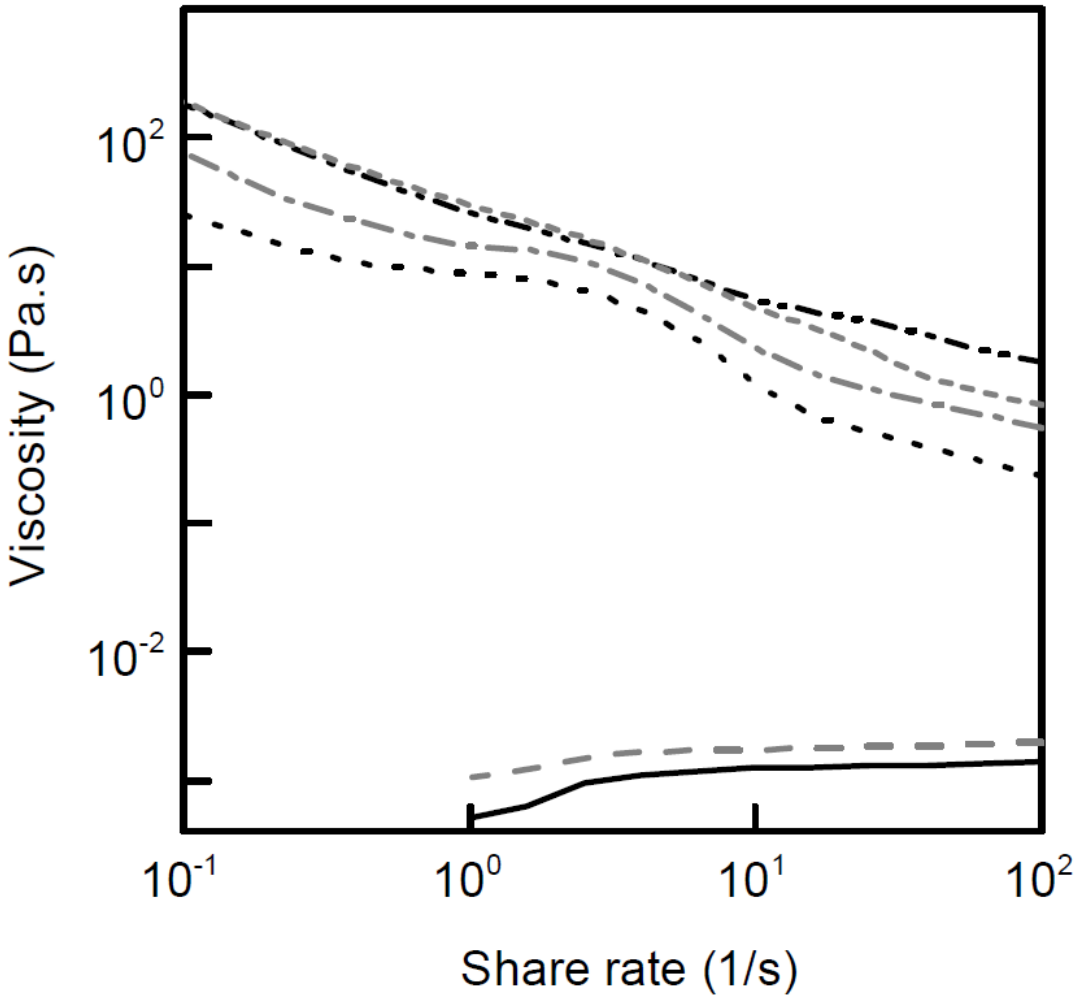

Figure A.7 Cup and bob measurement of nanocomposite gels formed with 1 w/v% of polymer and 15 wt% salt (polymer weight basis), nanocomposites: 150 kDa with 62% ENbn fraction. Day 1 (black solid line), day 2 (gray dash line), day 3 (black dot line), day 4 (gray dash dot line), day 5 (black dash dot dot line), and day 7 (gray short dash line).

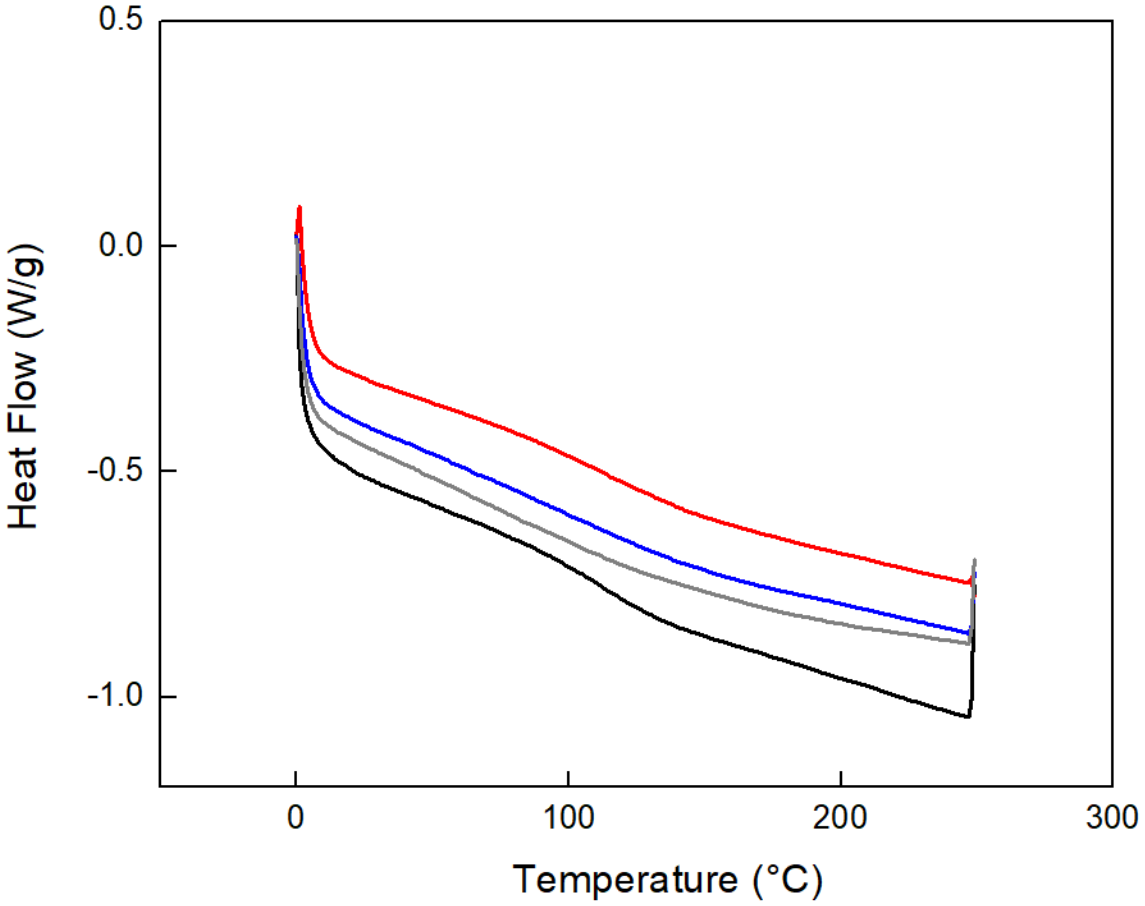

Figure A.8 Glass transition temperature of poly(lignin methacrylate)s via RAFT and free radical polymerization: PLM_1 (blue solid line), PLM_2 (gray solid line), PLM_3 (red solid line), and PLM_4 (black solid line).